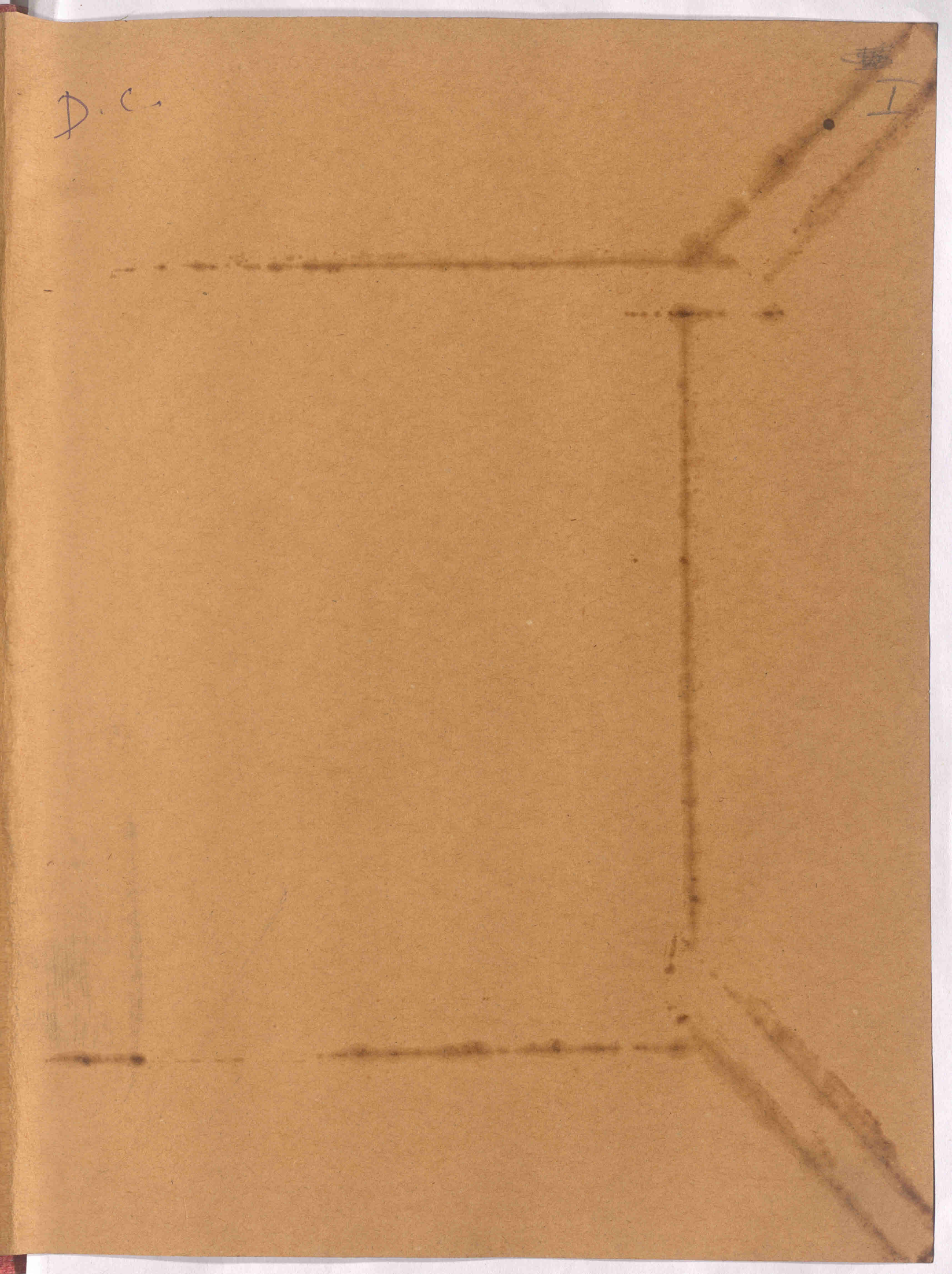
PHYSICO-CHEMICAL STUDIES AND DIELECTRIC BEHAVIOUR OF SOME CLAYS

RATISH KUMAR BEDI

THESIS SUBMITTED
TO
THE UNIVERSITY OF JAMMU, JAMMU
FOR THE
AWARD OF THE
DEGREE OF DOCTOR OF PHILOSOPHY
IN PHYSICS

1977



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C E R T I F I C A T E

Certified that the work presented in this thesis has been done under the supervision of Dr. S.N.Khosla, Reader in Physics, University of Jammu, Jammu. No part of this work has been submitted in part or full for a degree in any other University.

R.K.Bedi

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Certified that -

(i) the thesis embodies the work of R.K.Bedi and is worthy of consideration for the award of Ph.D. Degree;

(ii) the candidate worked for the period required under rules;

(iii) the candidate has put in the required attendance in the department during that period.

S.N.Khosla

(S.N. KHOSLA)
SUPERVISOR

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R.K. Bedi

(R.K. BEDI)

S Y N O P S I S

Nature has endowed the State of Jammu and Kashmir with vast and rich mineral resources, which for want of complete and consistant data with regard to their structure, composition and properties, could not be successfully exploited for the benefit of any clay based industry. Increasing developmental activities in the State and greater emphasize being laid on the utilization of regional resources for the industrial development of the region had compelling effect which motivated the author to undertake the studies on six clays from Jammu Province. The clay deposits at Parmandal which occur in three varieties and those at Jagati, Khanpur and Jungle Kali have been chosen for the purpose. The sites of these deposits are well connected by road and their estimated cumulative reserves fall around 8,00,000 tonnes.

Scope of the studies have been essentially kept limited to the extent of predicting the physico-chemical, mineralogical and electrical properties of the clay minerals so as to present a comprehensive data which may provide stimulous for further basic research or prove useful for any meaningful utilization of these, thus far, unassessed and unexploited resources.

Physico-chemical studies include the determination of properties like pH, slaking, swelling, the maximum and

minimum water of plasticity, plastic flow characteristics, workability, dry hardness, dry linear shrinkage, specific conductivity, specific gravity, heat of wetting, spalling resistance, mechanical and particle size analysis, besides viscous flow characteristics of clay suspensions of varying concentrations with and without the addition of electrolytes. Also, in addition to the temperature variation of colour, the fired characteristics, namely; density, porosity and shrinkage have been studied in the temperature range of 600 to 1100°C, the maximum temperature of the experiment.

Mineralogical investigations involve the identification of constituent clay minerals present in each sample as estimated from base exchange capacity, chemical, dehydration and differential thermal analysis data. X-ray and infrared techniques were also exploited for the purpose and the results supplemented to ascertain the mineralogical composition.

Electrical properties of clay compacts with reference to electrical conductivity, dielectric constant, dielectric loss and dielectric strength were studied with different soaking periods between 800 to 1000°C, the region in which fluxes melt, glassy phase appears and porosity approaches minimum. The corresponding changes in the density and porosity of the compacts were also recorded to correlate the results with the observed electrical behaviour.

Exceeding the limit and scope of the project primarily concentrated and directed to investigate the properties of only clays, a moderate attempt was also made to study the electrical, thermal and some mechanical properties of a triaxial system (clay; quartz: feldspar:: 2:1:1) using the only kaolinitic variety. The composition compacts pressed at 7000 psi were fired for 3 hours at 1150°C - the temperature around which soft porcelain or stone ware is usually prepared. The results obtained were correlated with corresponding density and porosity values.

Investigations reveal that all the clays are alkaline in nature, though the alkalinity varies from sample to sample. While clays from Parmandal, Jagati and Khanpur slake faster and show higher swelling, Jungle Kali sample is practically non swelling in character and takes much longer time to disintegrate completely. But for the too bottom layers of Parmandal deposits which are coarse, lean, less plastic and poor to work at, all other samples are fairly compact, fine in texture, and possess good plasticity and workability. Jungle Kali clay is the finest followed by top layer of Parmandal deposits, Khanpur and Jagati.

Fired properties like density, porosity and shrinkage show significant changes from around 800°C onwards, the exact temperature and the rate of change being dependent

upon the amount of fluxes, besides the particle size distribution of the individual sample. The fired colour of clays is found fairly compatible with the content of colouring agents like oxides of iron and titanium present in each case. But for Jungle Kali sample, all other clays vitrify around 1000-1100^{o}C.

Chemical analysis data give silica-alumina ratio comparable to bentonites for all clays, except Jungle Kali which appeared kaolinitic in character. Base-exchange capacity coupled with the swelling behaviour and chemical analysis data assert that with the exception of Jungle Kali sample all others are Ca-Mg based bentonites, though associated with small amounts of Sodium and Potassium ions. Dehydration, Differential Thermal, X-ray and Infrared analysis confirm that in these bentonites, montmorillonite is the principal mineral constituent, though in association with varying amounts of illite. Kaolinitic sample has kaolinite, quartz and illite in it. All the clays appear to contain small amounts of some other undetected clay mineral impurities also.

Electrical conductivity, dielectric constant, dielectric loss and dielectric strength of clays increases with the increase in temperature, as well as, soaking period presumably owing to the development of crystalline phase in the matrix. While the presence of titania enhances the

electrical conductivity depending upon the amount present in each sample, the deleterious effect of fluxes and beneficial effect of titania on the dielectric constant of clays has also been observed. With the exception of Jungle Kali sample, the two bottom layers of Parmandal deposits show comparatively higher electrical conductivity and dielectric loss which may be attributed to the presence of higher percentage content of alkalies in them. Iron oxide, however, decreased the dielectric strength of the specimens.

The variation in the physical properties, like density and porosity of the clay samples has shown good relationship with their electrical response.

In triaxial system studied with only one composition, although electrical and thermal conductivity results have been found fairly in agreement with the standard values reported, its dielectric, compressive and transverse strength is rather poor. Expansion contraction behaviour of the body composition shows the alpha-beta transition between 500-650^{o}C due to the presence of quartz. Also, the initiation of the formation of mullite phase has been observed at 1150^{o}C, as revealed by X-ray diffractogram of the fired material.

The thesis has been divided into five chapters dealing with (1) a brief introduction of the project,

plan of work and literature review, (2) experimental methods and procedures adopted during investigations, (3) observations, results and discussions on clays, (4) brief study on the triaxial system and (5) conclusions with general discussions, respectively.

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CHAPTER - I

INTRODUCTION, PLAN OF WORK AND LITERATURE REVIEW

1.1 INTRODUCTION:

Clays form one of the primary and most essential raw materials in number of industries like rubber, paper, paint, pharmaceutical, cement and ceramics. Large deposits of various types of clay minerals occur in the State of Jammu & Kashmir. Although, these deposits were explored long back and Geologists are still busy surveying to locate fresh ones, it is unfortunate that practically no attention has been paid in the past to characterise and evaluate even those discovered by Middle Miss, almost half a century ago. Consequently, even very rich and vast mineral resources of this region have either remained unexploited for use in industry or used to produce the products of doubtful quality.

With present tempo of development and industrial growth of this otherwise backward State, as well as, to meet the requirements of existing clay consuming industries in the neighbouring ones, which at the moment depend upon the supply of raw materials from places situated far away from the units, it is felt desirable to characterise some of the deposits of this region to pave way for their possible exploitation in industry. As a matter of fact, it will be more

appropriate and economic as well to develop clay-based industry in this region itself so as to utilize the available indegenious material rather than to depend upon the import of the products. Indeed any such move which is directed towards the evaluation of raw materials will not only help accelerate the pace of industrial development of the State while consuming its own resources but also increase the employment potential and contribute towards an overall welfare of the people of the region.

From the point of view of consumption of the products, if manufactured locally, there exists enough demand for house-hold crockery and other soft porcelains in the State. In addition to this, Jammu and Kashmir being on the tourist map of India attracts heavy influx of tourists running into millions every year - a factor which can provide an additional market for decorative products also. Further more, with the coming up of Salal and other hydroelectric projects in the region, there will be an ever increasing demand for ceramic insulants needed for the transmission and distribution of electrical energy.

It is indeed, in view of above considerations that it is planned to evaluate some of the mineral deposits, particularly those situated in Jammu region,

with their estimated reserves well over 8,00,000 tonnes. These deposits are well connected by road to National High Way and the rail head at Jammu. Investigations to be carried out are broadly categorised under two headings, namely; (i) characterisation which will include the determination of physico-chemical and mineralogical properties and (ii) electrical response involving studies on the electrical conductivity, dielectric loss, dielectric constant and breakdown voltage of clays. It may be emphasized here that no consistant work has been done, till data, even to establish the character of these deposits. It is believed that the investigations will not only reveal thus far unestablished nature and character of these deposits, but also provide basic data which may act as an indicator for their possible utilisation in various clay-based industries. Needless to mention that most essential prerequisite for the application of a clay mineral in any industry is to know and understand its physical, chemical and mineralogical characteristics besides electrical, thermal and mechanical response.

1.2 PLAN OF WORK:

The physico-chemical properties of clays proposed to be studied are; the colour at room and upto around vitrification temperature, pH, slaking, swelling

specific conductivity, dry linear shrinkage, dry strength, heat of wetting, spalling resistance, besides maximum and minimum water of plasticity and other plastic flow characteristics. Further, the studies on the viscosity of clay suspension of various concentrations and the effect of addition of electrolytes is included to have information regarding the role played by the ions associated with the latter in changing the viscous flow characteristics of the former. Particle size analysis of the samples will represent the percentage of particles present in different size ranges and enable to assess the clay content in each sample. Mechanical analysis will also help in this direction, particularly to know the percentage of particles having size greater than that of clay i.e. the fraction of silt and sand. Indeed, the studies on the particle size distribution have significant effect on and bear close relationship with the properties of clay minerals both in their raw and fired state.

Cation exchange capacity measurements provide useful information to ceramists regarding the nature of minerals in a clay and to identify the latter. Montmorillonites and even some finely grained illites absorb and hold cations by weak electrical forces due

to the charge deficiency within the lattice. One can customarily distinguish between clays according to the type of cations they predominently absorb. Chemical analysis data will add to this and reveal various chemical constituents present in a clay, such as, the amount of fluxes, alumina and silica etc. This information not only helps though in a limited way, to identify the type of the principal mineral present in a clay, based upon its silica-alumina ratio and the presence of other constituents; but also acts as an indicator to assess the behaviour of the material at high temperatures. Firing characteristics, e.g; density, porosity and shrinkage are discussed in view of the role played by fluxes and other chemical constituents present in the samples, in addition to the particle size distribution in them.

In order to identify various constituent minerals present in each clay, mineralogical studies are proposed to be carried out. Since clays are generally considered to be admixture of various minerals, it is considered unreliable to derive conclusions based upon the results obtained using only one or two techniques available for the purpose. In the present work it is proposed to carry out the mineralogical analysis through dehydration, differential thermal, x-ray, infrared techniques, and supplement the results obtained in each case with a view to know

mineralogical composition of materials, as best as possible.

Electrical response such as electrical conductivity, dielectric loss, dielectric constant and dielectric strength will be presented for clay compacts pressed at 5000 p.s.i. employing different soaking periods, in the temperature range of 800 to 1000°C. This temperature region has been chosen for the simple reason that fluxes which are present in clays and effectively control the electrical properties melt in this temperature range. The corresponding changes in physical properties like density and porosity of compacts will also be measured and results correlated with the observed electrical behaviour.

Thus, the proposed plan presents a well coordinated approach adopted to characterise six clay mineral deposits as mined and also study their electrical behaviour to have an indication for their possible utilisation in insulator or any other related industry. Indeed, it is a first attempt of its kind in which such a comprehensive data on Jammu clays has been provided, with a view to exploit the resources for the development of clay-based industry.

1.3 LITERATURE REVIEW:

Of all the properties exhibited by ceramic materials colour is most fascinating, impredictable and

difficult to reproduce with precision in fired ware. Colour of natural occuring clays vary over a wide range. While Rajula bentonite is pale white occasionally having greenish, buff and light brown patches[1]; those from Jodhpur, Karule, Akli and Hathi-Ki-Dhani show ferrogenous impurities after firing. Henry[2] described different compositions of oxides of elements which impart colour to the ceramic materials. Ghosh and Sen[3] studied the fired colour of clays in relation to their Fe_2O_3 and TiO_2 content. pH of a clay indicates its alkaline or acidic nature. It has been attributed to the presence of hydrogen, at least in part, as exchangeable cations in a sample. pH values of some Indian clays have been reported[4,5]. Yodar[6] attributed slaking to the increase in the thickness of absorbed water film and expansion of the clay minerals. It is believed[7] that slaking can be decreased by electro-osmotic and electro-chemical treatment of a clay and also by the introduction of organic cations which develop hydrofabric qualities in it. Clays slake more readily in water than well laminated shales. The better the orientation or lamination, the poorer the slaking properties[8].

Swelling of a clay depends upon the amount and type of soluble salts and the minerals present

in it. It has been demonstrated[9] that the extent of adsorption is strongly dependent upon the nature and concentration of associated ions. Bentonites show higher swelling whereas kaolinites give very low values[10]. Sen Gupta[11] studied the swelling behaviour of different bentonites from Jodhpur. Some Indian bentonites[12] reveal conchoidal or subconchoidal fracture compatible with the observations of Beach and Francis[13]. Davies and Vacher[14] showed that even 2% salt solution reduces the swelling markedly. Effect of sodium carbonate treatment on the swelling behaviour of some Indian clays has also been reported[15].

It has been suggested that dry linear shrinkage of elongate and fibrous clay minerals is relatively large; also, coarser particle dry more readily than the finer[16]. Kaolinites[17] show very low dry linear shrinkage as compared to bentonites. It has also been shown[18,19] that in kaolinitic clays the amount of shrinkage decreases in the order of H,Ca,K and Na.

Anonymous[20] concluded that dry strength of clays is closely related to their particle size. The presence of adsorbed sodium ions is believed[21-23] to enhance the dry strength values than do the other common cations. However, the interactions between the

exchangeable cations have been thought to produce gelatinous precipitates at particle contacts, lowering the strength[24]. An increase in the dry strength was observed[25] with lower porosities and higher packing densities. But Weymouth and Williamson[26] concluded that these factors do not always decrease the strength. In a plastic clay it may be influenced by the water content also[27-29].

Barna[30] defines the plasticity as the ratio of the shrinkage water and the water of plasticity. Whittemore[31], however, implies water of plasticity as the amount of water to develop the plasticity of a clay and to bring it to a good workable consistancy. Clay workers, generally, consider it as an index of plasticity[32]. Norton[33] observed that plasticity of a clay varies with its water content. Worrall and Khan[34] concluded that the plasticity indices are independent of moisture content over a wide range. Plasticity of a clay is considered[35,36] mainly due to the platy nature and fineness of its particles. Baver and Winterkorn[37] indicated a close relationship between the water affinity and plasticity index. Hauser and Johnson[38] discussed plasticity of clay from colloid physical stand point. Das et al[39] studied the workability of Indian bentonites. It is observed that calcium or magnesium based clays

are better to work at than sodium or potassium ones. Prasad et al[40] asserted that clays having good workability may not have high bonding power.

The dependence of viscosity of a dispersed system on the volume concentration of particles in it has been theoretically calculated by Einstein[41] and Mooney[42]. The reduction in the apparent viscosity on adding NaOH and Na_2SiO_3 has been discussed by various workers[43-45]. Recent work in colloidal chemistry[46] indicate that the suspended particles are in equil-ibrium between repulsive and attractive forces and this equil-ibrium can be varied by adding ions. Organic matter[47], the size and shape of the particles[35] also greatly influence the viscosity. Bose[48] studied the effect of various electrolytes on the flow properties of Rajmahal kaolinite. Guha et al[49] established a direct relationship between the nature and quantity of organic matter and the casting properties of clays. Flow characteristics of ceramic clays studied by Hen-ry and Taylor[50] show relationship between the chemical composition and their physical behaviour.

Various authors[51-53] determined the particle size of clays based upon the principle of settling of suspension by gravity or by centrifugal forces. Jacobsen and Sullivan[54] successfully employed centrifugal

method which was later used by Mandal and Lahiri[55] for determinining the size distribution of finer particles in Indian ceramic clays. Some authors[56,57] employed Andreasen pipette method for determining particle size distribution using water as settling medium. Roy[58] concluded that the proportion of fine particles in china and fire clays is less than that in bentonitic and illitic varieties. Banerjee and Chatterjee[59] has studied particle size distribution of some Indian clays. Abdel Aziz et al[60] found the linear relationship between the logarithim of the particle size and probability of cumulative percentage of some Egyptian kaolinities. Dinsdale and Wilkinson[61] related the technological properties such as porosity, density, shrinkage, strength etc. with the particle size distribution of the raw materials.

Chemical analysis of clays has been carried out by various investigators using different techniques. In Dion's[62] approach geothite can be quantitatively removed from clay under controlled conditions. Although SiO_2/Al_2O_3 ratio obtained from chemical analysis of a clay may indicate its approximate refractory value, yet this ratio has limitations and can not be relied as criterian to identify specific mineral present in a clay[63]. Bennett[64] described a method in which silica is

determined by combined gravimetric and spectrophotometric method. Although the determination of silica by precipitation as potassium flurosilicate has been suggested[65,66], yet it is not considered[67] applicable to most materials due to the interference of elements like aluminium and titanium. Mitra et al[68] have reported a method for the determination of total iron content in silicate materials. Sen[69] has described a quick method for simultaneous estimation of silica and alumina in alumino-silicates.

The base exchange capacity of clays determined by different investigators varies widely. Grim[70] has given the range of bec values of different clay minerals. Samson et al[71] observed different cec values when measured by Kjeldahl distillation of ammonium montmorillonite and photometrically by displacing sodium ions. According to Johnson and Norton[44], only positive active areas absorb OH ions preferentially which are firmly held by the particles as if they are an integral part of the solid. Dion[62] demonstrated that Fe_2O_3 reduces the cec of clay minerals by clogging action. The removal of organic matter from clays by low temperature oxidation also effects cec[72]. Kelley and Jenney[73] stated that cec of well balanced kaolinite mineral, if explained on the basis of broken bonds alone,

give rise to smaller values. It was suggested[74] that the possible adsorption sites may arise at the edge of kaolinite layer. Kaolinite and illite show an increase in cec with the decrease in the degree of crystallinity[75,76]. While higher cec of Travancore and Rajmahal china clays[77] is attributed to the presence of mica in them, Ratija sample is believed to show high cec due either to its disordered nature having charge deficiencies or the presence of illite in it having higher exchangeable ions[78].

Baver and Wintercorn[37] have emphasized the importance of the development of orientation of water molecules in the adsorbed water as the cause of heat of wetting. Janert[79] was of the opinion that ion hydration is a major cause of heat of wetting, while Siefert[80] referred surface to be more important than cation hydration. It was suggested[81,82] that heat of wetting varies with the adsorbed cations. Harmon and Fraulini[75] have presented data showing an increase in heat of wetting of kaolinites with decrease in particle size, whereas no such correlation could be established in case of montmorillonites. Heat of wetting of Indian clays have not been reported by any worker.

Satisfactory performance of refractories in many applications depends critically on the spalling resistance[83-85]. Hasseleman[86] and Buessum[87] indicate the dependence of spalling resistance on the rate of heating, heat flux or temperature gradient. Pevzner[88] measured it in terms of loss in strength or weight, change in elastic behaviour or number of cycles required for complete failure of the material. It has been suggested[89] that too high or too low porosity of fire clay deteriorate their spalling resistance.

ASTM has established that bulk density of grains can be determined either by immersion in boiling water[90] or mercury displacement[91]. Ruprecht[92] concluded that a method using two minutes immersion in water is applicable to all principal refractories. It was stated[93] that the density of relatively large aggregates can be determined using mercury balance, where owing to the high contact angle of mercury penetration in the open pores does not occur. For porosity measurements standard mercury porostimeters have been described and discussed[94,95]. Mukherjee[96] demonstrated that the nature of raw material, size distribution, mixing, grading, methods and techniques of firing greatly influence the fired porosity of the samples. A number of investigators[40,97,98] have studied the fired properties of Indian clays.

Various techniques have been employed to study the dehydration characteristics of clay minerals. Work of Nutting[99], Ross and Kerr[100,101] and Kelley[102] is note worthy. They studied the dehydration properties by heating clay minerals at different temperatures till no loss in weight occur. Ross and Kerr[100] showed that kaolinites and illites lose very little water upto 400°C and 600°C, respectively; while in montmorillonites, the rapid loss of OH water begins at 500°C. However, dehydration is complete in all clay minerals around 800/900°C. Puri[103], Kuron[104] and Alexander and Haring[105] plotted dehydration curves of water content versus vapour pressure. Brindley and Nakahira[106] also studied the role of water vapours in the dehydroxylation of clay minerals and showed that size, shape and packing density influence the dehydration rate. Cold Well and Marshall[107] studied the effect of particle size on the dehydration characteristics of montmorillonites and also showed that irreversible dehydration depends upon the exchangeable cations present. Dehydration behaviour of Jodhpur and Karauli bentonites has been reported[108].

Differential thermal technique of analysing constituent minerals in clays has been widely used. Grim and Rowland[109] identified the minerals on the basis of appearance and temperature of the peaks in D.T.A.

curves of many binary and tertiary mixtures of kaolinites, illites and montmorillonites. Tiny peak at 150°C was attributed[110] to disordered fine grained kaolinite, while its absence to nacrite, dickite or coarse grained kaolinite. Poorly crystalline kaolinites show[111] peak temperature lower than that for well crystallized variety. It is believed[112,113] that fluxing impurities suppress the exothermic peak in kaolinites. Various investigators[114-116] observed the appearance of characteristic endothermic peak in Indian bentonites at temperatures lower than for montmorillonites. Speil et al[117] studied the differential thermal curves of mixtures of kaolinite and montmorillonite in different proportions and observed dual peaks at 580°C and 712°C. Roy[118] calculated area of the peak due to dehydroxylation and related it with the surface area. It has been suggested[119] that the nature and the temperature at which exothermic peak appears at high temperatures depends upon the extent of substitution of Al^{+3} in the tetrahedral position and the resulting phase that appears.

Non destructive technique of x-ray analysis has been extensively employed for identification of mineral constituents in clays. Bradley et al[120] and Mac-Ewan[121] made significant contributions in applying this technique in clay mineralogy. According to

Greene-Kelley[122], in montmorillonites, structural change arises mainly from the octahedral layers. The basal reflections of montmorillonites vary from 9.4A°-14A° which, generally, appear very broad and diffused and depend upon the exchangeable cations present[123]. The essential characteristic of kaolinite pattern is manifested in the group of triplets 2.55, 2.52, 2.49 A° and 2.37, 2.33, 2.28 A°. Illite gives a first order reflection of 9.9-10.1 A°. It has been pointed out[124-126] that the position of (060) reflection and the intensity of the second order basal reflection can usually be used to distinguish between dioctahedral or trioctahedral layers. Grim and Bradley[124] studied the effect of major substitutions in the mica lattice and the intensities of (001) reflections. According to Grim[127], in a random interstratification of primary mineral with only a few layers of the second mineral, the x-ray diffraction pattern will differ very little from that of dominent mineral. Random, as well as, ordered interstratification of illite and montmorillonite layers in bentonite has been established through x-ray technique[128-130]. Interstratifications of biotite and chlorite, vermiculite and chlorite, montmorillonite and chlorite have also been reported[131]. Searle and Grim-shaw[132] tabulated the interlayer spacings and the corresponding intensity of different clay and non clayey minerals.

Infrared spectroscopy provides in it a quick method for identification of clay minerals. It has been suggested[133] that the best spectra are obtained with sample having a narrow particle size distribution. The absorptions in the ranges of 2.7 to 3.2 micron and 6.0 to 6.2 micron are assigned[134] to hydroxyl and hydrated water respectively. A careful study[135,136] of dehydration behaviour of series of montmorillonites indicate that the characteristic absorption at 2.75 micron represents the presence of lattice hydroxyl called unbonded or free hydroxyl because of its crystallographic similarity to the hydroxyl of the strong alkali metal bases. Keller et al[137] have described the band between 9 to 10 micron due to SiO_4 group, although conclusive distinction between absorptions due to silica tetrahedra and aluminium octahedra has not yet been made. Montmorillonite, illite and muscovite show the characteristic absorption peaks between 9 to 10 micron, while kaolinite and halloysite is identified in the range 10 to 11 micron. Usually montmorillonite and illite, when present together are difficult to distinguish[134] as their characteristic peaks are very close and lie at 9.6 and 9.7 micron, respectively.

Mineralogical investigations of Indian clays from different parts of the country have been

carried out by a number of workers[138-153] mostly employing D.T.A., X-ray and I-R techniques.

With the development of ceramic insulator technology in the recent past the studies on the dielectric properties of the materials has attracted a large number of workers in its fold all over the globe. Inspite of tremendous work being done in this area of study, it is hard to say that the various factors and mechanism controlling the dielectric behaviour of materials has been completely understood.

Specific resistivity of magnesia, porcelain and refractory oxides at elevated temperatures has been reported[154-155]. Northrup[156] suggested that electric conduction in refractories is both electronic and electrolytic at elevated temperatures. Werner[157] found no regular relationship between porosity and the resistivity and asserted that fluxes decrease the resistance markedly. Wallace and Ruh[158] reported the change in electrical resistivity with temperature for a number of refractory materials. Ford and White[159] attributed the different resistivity values of ceramic materials to the configuration and defects within the lattice. Kraner[160] emphasized that interpretation of electrical conductivity of refractory materials cannot be done solely on the basis of chemical and mineralogical

composition of the sample. It is suggested[161,162] that impurities and even technological parameters influence conduction phenomena. Electrical measurements made on ceramic materials at room temperature show[163-165] that porous bodies may give erroneous results unless they are thoroughly dry. TiO_2 which is known as reduction semiconductor decreases the resistance[166,167]. Weyl and Forland[168] believed that the introduction of relatively small number of fine valence cations cause the reduction of an equal number of Ti^{+4} to Ti^{+3} thus preserving the electroneutrality of the lattice. Bryson[169] and Sutton and Silverman[170] have shown that the electrical resistance of glass drops almost in direct proportion to the decrease of viscosity with rising temperature. It was stressed[169] that even 5% of alkalies, which enter porcelain through feldspar, rapidly decrease the resistivities. The microscopic study of insulators[171,172] reveal microcracks in the glassy phase and in quartz grains. Rigterink[173] demonstrated that materials with strong covalent bonding and lesser number of ionic carriers show excellent dielectric properties and asserted that electrical properties improve with the improvement in microstructure.

The dielectric loss of the materials, generally, improve[174] as the alumina content increases

and the glass content decreases. The temperature at which an insulator will fail under any particular voltage gradient has also been predicted from temperature resistivity curves[174]. Von Hippel[175] reported that in crystals, the dc break down strength increases with temperature in low temperature region, while it decreases in case of amorphous materials. The mechanism of dielectric break down strength of different types of solids have been explained on the basis of electronic processes[176,177]. In porcelains, strength increases greatly when alumina is substituted for flint[178]. The effect of variations in the fineness of quartz and feldspar on the dielectric strength of electrical porcelains has also been studied[179]. It is believed that size of specimen, shape[180] and porosity[181] also affect its dielectric strength.

Guha[182] studied some Indian clays to assess their suitability in electro porcelain bodies. The use of Indian talcs for the manufacture of low loss insulators and steatite bodies has also been reported[183, 184]. Clays from Kerala region[185] have been found suitable for electrical porcelains. Choudhary[186] has worked on the electrical insulants making use of an Indian china clay.

CHAPTER -II

EXPERIMENTAL METHODS AND PROCEDURES

This chapter deals with the experimental techniques employed during the course of investigations. For the sake of convenience, it has been divided into three parts relating to the methods and procedures adopted while determining (i) Physico-Chemical, (ii) Mineralogical and (iii) Electrical properties of clays which have been discussed separately in sections 2.1, 2.2 and 2.3, respectively.

Six clay samples, 50 Kg each, were collected for investigations at the site of the deposits through the courtesy of the Department of Geology and Mining, J&K Government, Jammu. The clay minerals collected include three varieties of Parmandal deposits and those occuring at Jagati, Khanpur and Jungle Kali. As these samples were available in the form of lumps of varying size, they were crushed to small pieces and further sampling done in the laboratory according to the procedure laid for the purpose. Each clay sample was powdered to pass through 120 ASTM sieve and the material stored in separate containers for further use. The laboratory number was assigned to each clay as given below:

Parmandal deposits (top layer) --- Cl-1

Parmandal deposits(middle layer) --- Cl-2

Parmandal deposits(bottom layer) --- C1-3

Jagati deposits --- C1-4

Khanpur deposits --- C1-5

Jungle Kali deposits --- C1-6

2.1 PHYSICO-CHEMICAL PROPERTIES:

This section has been divided into two sub-sections 2.1.1 and 2.1.2 dealing with General and Fired properties, respectively.

2.1.1 General Properties

The section covers the determination of properties like, colour, pH, slaking, swelling, water of plasticity, specific conductivity, heat of wetting, spalling resistance, mechanical analysis, particle size analysis, viscosity, specific gravity, base exchange capacity and chemical analysis.

(i) Colour:

The material in the form of powder (-120 ASTM) was examined visually for colour at room temperature. Also, the change in colour with temperature was recorded upto 1100°C. The dominent colour was assigned to each sample as per specifications laid down by Indian Standard colours for ready mixed paints.

(ii) pH:

15 gms of dried powdered material was added to 150 mls. of distilled water and the mixture

given a continuous shaking for 3 hours with an electric stirrer operated at 3000 RPM. pH of the suspension was measured with phillips precission pH water PR-9405; M/90. The buffer solution used in the measurements had 8.4 pH and was prepared by dissolving the standard tablet in 100 c.c. of distilled water without shaking.

(iii) Slaking:

Cubes of approximately 2 cm side length were prepared from the plastic mass and dried at 110°C for 2 hours. One by one, each specimen was kept on the top of IS sieve 270, placed in the water-bath maintained at 30°C and the time taken by it to disintegrate completely noted. Five test specimens of each clay were used and the average slaking time recorded.

(iv) Swelling

10 gms of dry powdered material (-120 ASTM) was transferred to a graduated cylinder so that no particle sticks to its sides and the level of the clay column noted. A measured quantity of distilled water eight times the weight of the sample, was then slowly added without disturbing the clay column. The cylinder, covered with glass disc, was allowed to remain at rest for seven days to permit the swelling of the clay. Increase in the level of clay column was noted after every 24 hours to give maximum swelling in c.c/gm.

The procedure was repeated thrice for each sample and average value recorded.

(v) Dry Linear Shrinkage:

Two parallel lines, about 2 cms apart, were drawn on the face of the tablets, three for each clay, prepared from the plastic mass and when they acquired some rigidity after being exposed to the atmosphere. The distance between the lines was measured under travelling microscope. The specimens were dried at 110°C in a muffle furnace for four hours and the distance between the lines remeasured and average percentage of shrinkage for each clay calculated.

(vi) Dry Strength:

Samples (approx. 4x1x1 cms) were cut directly from lumps using a sharp knife and their faces grounded with 0000 emery paper. These samples were dried at 110°C and placed over two wedges situated at about 6 cms apart. A uniform pressure was applied at the centre of the top surface by third wedge. Pressure was increased slowly till the test piece broke down. Modulus of rupture in lbs/inch^2 was calculated using the relation

$$T = \frac{3\,WL}{2\,BT^2}$$

where W is the breaking load in lbs; L, the span length; B and T, the breadth and thickness of the specimen,

respectively. Average value of five samples of each clay was recorded.

(vii) Water of Plasticity:

To a known quantity of dried material was added distilled water, drop by drop, till it formed a plastic mass which could easily be moulded to any shape. Cubes of approximately 1.5 inch side, prepared from the plastic mass were weighed and dried at 110°C till there was no loss of weight. The weight of the dried sample was recorded and the maximum water of plasticity calculated as the mass of water in grams required to make 100 gms of clay plastic.

For minimum water of plasticity, a known quantity of the plastic mass was rolled on a glass plate, applying uniform pressure by hand, to form a thread. The process was repeated till the rolling of the mass into thread was no longer possible. The crumbled mass was weighed and dried at 110°C to a constant weight. The loss in weight per 100 gms of the clay was calculated to give its minimum water of plasticity.

The above tests were performed thrice for each clay sample and average value of plasticity recorded.

(viii) Plastic Flow Characteristics:

Atterberg apparatus was used to determine

plastic flow characteristics while adopting the following procedure:

(a) Liquid limit and Flow Index.

120 gms of the sample (-250 micron) was dried at 110°C for two hours and mixed with distilled water to form a plastic mass. A part of the mass was placed in the cup of the apparatus and squeezed and spread at its bottom. While applying the minimum number of spatula strokes the mass was simultaneously trimmed to a depth of 1 cm. at the point of maximum thickness. The mass in the cup was then divided by a firm stroke of a grooving tool along the diameter of the cup and through the centre line of the cam-follower, so as to get a clear and sharp groove of uniform dimensions formed in the mass. The cup was lifted and dropped alternatively by turning the crank at the rate of two revolutions per second and number of strokes recorded when the two halves of the plastic cake came into contact through a length of about 1 cm. Finally, a representative slice of the cake, cut at right angle to the groove including the position in which the two halves colasceased, was taken and its percent moisture content determined. The above operation was repeated thrice for each sample and the average value of the moisture content recorded.

A curve was plotted on the semi-logarithmic

graph between the water content on arithmatic scale and number of drops on the logarithmic scale. The moisture content corresponding to 25 drops was recorded as the liquid limit of the sample.

The above curve was extended to intercept the ordinates corresponding to 10 and 100 drops. From the slope of the line, expressing the difference in the water content at 10 and 100 blows, the flow index was calculated using the relation.

$$\text{Flow Index} = W_1 - W_2 / \text{Log}_{10} N_2 / N_1$$

Where W_1 and W_2 represent the moisture content in percent corresponding to $N_1 = 10$ and $N_2 = 100$ blows, respectively.

(b) Plasticity index and Toughness index.

Plastic mass of 120 gms of the material (-425 microns) was prepared using distilled water and allowed to rest for 24 hours so that water could permeate through it. A ball of plastic mass weighing 10 gms. was rolled between the fingers and a glass plate, applying uniform pressure, to and fro, forming a thread of same diameter throughout its length. The rate of rolling was kept about 80 strokes per minute. The rolled mass was kneeded together and the process of rolling and kneeding repeated till the mass could no longer be rolled into thread. The percentage moisture

content at this stage was determined to give the plastic limit.

While the difference between the liquid and plastic limit was taken as the plasticity index, the ratio of the plasticity index to flow index recorded as toughness index.

(c) Liquidity index and Consistancy index.

These indices were calculated using the relations

$$\text{Liquidity Index} = W_o - W_p/I_p$$

$$\text{Consistancy Index} = W_1 - W_o/I_p$$

where W_o is the moisture content; W_p and W_1, the plastic and liquid limits respectively; and I_p, the plasticity index of the clay.

(ix) Viscosity:

Viscosity of the clay suspension was measured using Ostwald Viscometer. Clay suspension of known concentration in distilled water was poured into the left limb having narrow capillary section along a part of its length. The time taken for the level of the suspension to fall between two arbitrary marks R_1 and R_2 was noted and viscosity determined using the relation

$$\eta_2 = \eta_1 \frac{t_2}{t_1} \frac{\rho_2}{\rho_1}$$

where η_2 and η_1 are the viscosities of the clay

suspension and water, respectively; t_1 and t_2, the time taken in seconds by suspension and water level to fall from mark R_1 to R_2; ρ_2 and ρ_1 are the densities of the specimen and water, respectively.

Flow curves were plotted between viscosity and clay concentration. Following the same procedure, the effect of different concentrations of electrolytes (sod. carbonate and sod. silicate) on the viscosity of clay suspension was also determined.

(x) Particle Size Analysis:

5 gms of clay powder (-40 ASTM) dried at 110°C for 2 hours was taken in a flask containing 200 mls. of distilled water and 10 mls. of sodium pyrophosphate solution (24.55 gms. dissolved in 500 mls. of water). The flask was kept at rest for 24 hours before its contents shaken for 17 hours by an electric stirrer to ensure the dispersion of clay. The dispersed medium was introduced in Andreasen apparatus and the volume maintained to the upper mark provided, by adding more of distilled water. The cylinder was shaken for five minutes and placed at rest. 10 mls. of the suspension was taken out with the pipette at time intervals of 2,5,10,30,60,120,240,360,1440 and 2880 minutes and each fraction evaporated separately to dryness at 110°C. The percentage weight of the dried material

of each fraction was noted and the particle size calculated applying stokes law:

$$r = \sqrt{9hy/2(d_1 - d_2)\, gtx10^4}$$

where r is the radius of the particles in microns; h, the height of the suspension in cms; y, the viscosity; d_1 and d_2, the density of clay and water, respectively; t, the time in seconds and g, the gravitational force (961 cms/sec.^{2}).

(xi) Mechanical Analysis:

20 gms of a clay sample dried at 110°C was taken in a beaker with 60 mls. of 6% solution of H_2O_2. The beaker was heated on water bath keeping its contents stirred to avoid frothing. When the mass became thick, it was cooled; more of H_2O_2 solution added and the mixture reheated. This alternate heating and cooling treatment was repeated, every time adding H_2O_2 solution, till most of the organic matter got oxidised. Then, 25 mls. of sulphuric acid was added and the mixture filtered through Buchner funnel, using Whatman filter paper No. 50. The residue was washed with hot water and transferred to IS sieve 70 and rewashed with a jet of hot water until the clay particles could no longer pass through the sieve. The residue in the sieve was dried, weighed and its percentage calculated.

In order to separate the silt and clay fractions the filtrate from sieve No.70 was diluted to 1000 mls. in a cylinder; shaken well and placed at rest. After 216 seconds, 25 mls. of the suspension was taken out from a depth of 10 cms. below the top level. The suspension was dried, ignited and weighed to give the percentage of silt and clay together. Again, 25 mls. of suspension was removed after 6 hours and 20 minutes and the above procedure of drying, igniting and weighing repeated. The difference of the two percentages so calculated gave the percentage of silt.

For fine aand content, the supernant liquid was decanted off and the sedimented column transferred to 400 mls. beaker to which water was added to bring the column upto 10 cms. from the base. The beaker was allowed to rest for 216 secs. and the turbid suspension poured out. This process of adding and pouring out water was repeated till the suspension became colourless. The residue was dried, weighed and percentage weight calculated.

(xii) Specific Gravity:

A clean and dry specific gravity bottle was weighed (W_1) alongwith its stopper. Powdered material (-120 ASTM), previously dried at 110°C, was put into it and re-weighed (W_2), to give ($W_2 - W_1$),

the weight of the powder. Bottle was then carefully filled with kerosine oil and the weight of oil added (W_3) noted. Finally, the weight (W_4) of the bottle filled with only kerosine oil was taken and the true specific gravity calculated using Archemedes Principle.

(xiii) Specific Conductivity:

A known quantity of powdered material (-120 ASTM) dried at 110°C was mixed with distilled water in 1:15 ratio. The mixture was given a continuous shaking for two hours with an electric stirrer operated at 3000 RPM and the specific resistance of the suspension measured in mhos/cm, using Philips conductivity bridge. The reciprocal of the observed resistance was recorded as the specific conductivity. Experiment was repeated thrice for each clay and average conductivity recorded.

(xiv) Heat of Wetting:

10 gms of the powdered material (-120 ASTM) dried at 110°C was transferred to a copper calorimeter containing 50 c.c. of distilled water. The increase in temperature of the water was measured using Cu-Fe thermocouple. Heat produced per gram of the material was calculated thrice for each clay to record the average value. Correction for water equivalent of the calorimeter was applied in each observation.

(xv) Spalling Resistance:

Circular pellets of 25 mm dia and 3 mm thickness, prepared from the plastic mass and dried at 110°C were introduced in a furnace maintained at 1000°C. The pellets were removed after 10 minutes and allowed to cool at room temperature for the same period. The heating and cooling cycles were repeated till cracks appeared on the sample. The number of cycles when cracks initiated in each case was recorded as its spalling resistance. Three samples of each clay were used to get average number.

(xvi) Chemical Analysis:

0.5 gms of powdered sample was dried at 110°C for 2 hours and fused with 3 gms of Na_2CO_3 in a platinum crucible. The fused mass was transferred to a beaker using acidified water, and evaporated to dryness. The residue was washed with acidified water till free from chloride and the filtrate (1) kept for further observations. The residue was dried and weighed (W_1). To estimate silica content the residue was treated with HF and dried number of times. In order to avoid loss of titania, 2-3 drops of 1:1 H_2SO_4 was also added each time alongwith HF. Finally, the weight (W_2) of dried residue was noted and ($W_1 - W_2$)

recorded as the silica content in the sample. The remaining mass was then fused with potassium pyrophosphate; transferred into filtrate (1) and volume made to 250 mls.

50 mls. of the above solution was acidified with 2-3 drops of concentrated HNO_3 and heated. To this was added 2-3 gms of NH_4Cl; solution boiled for 3-4 minutes and cooled before adding methyl red (2-3 drops) and few drops of NH_4OH. The solution was allowed to stand for one hour for precipitation. It was then filtered through Whatman filter paper No. 41; ignited to give a constant weight and filtrate (2) kept for further tests. The ignited residue which contains ferricoxide, titania and alumina was weighed.

(a) Determination of Fe_2O_3.

The residue was fused with potassium pyrosulphate and the mass dissolved in 1:10 H_2SO_4 to make the volume of the aliquot (3) to 250 mls. To 100 mls. of this, $KMnO_4$ solution was added drop by drop till it gave pink colour. To this solution, 10 mls. of 1:1 HCl was added and evaporated to about 10 mls. before adding 20 mls. of concentrated HCl; heated to 50-60^oC and $Sncl_2$ solution was then added drop wise till the solution became milky. 10 mls. of

$HgCl_2$ and 10-15 mls. of a mixture of H_2SO_4 and H_3PO_4 (1:1) was added to milky solution which was then titrated against 0.01N solution of $K_2Cr_2O_7$ using diphenyl amine sulphonate as an indicator. The percentage of Fe_2O_3 present in the sample was calculated.

(b) Determination of TiO_2.

25 mls. of aliquot (3) was taken in Nessler's cylinder (A). Blank solution was prepared in cylinder 'B' with 5 mls. of 1:1 H_2SO_4, 1 ml. of phosphoric acid and 2 mls. of H_2O_2. Standard titania solution was prepared by fusing 0.5 gms. of pure calcined titania with potassium pyrosulphate at low temperature; fused mass was cooled; 6 mls. of concentrated H_2SO_4 added to it and the volume was made 500 mls. with distilled water. The standard solution of titania so prepared was added in cylinder 'B' until the colour of solution in it matches with that in cylinder 'A' and the percentage of TiO_2 determined.

(c) Determination of Al_2O_3.

Alumina present in the sample was determined by difference.

(d) Determination of CaO.

To 50 mls. of the solution (2) was added 10 mls. of triethanol amine and 5 mls. of 5N NaOH.

Mixture was titrated against .01M, EDTA solution using 0.2 gms. of Patton and Reade (P&R) as an indicator and percentage of CaO calculated.

(e) Determination of MgO.

To 50 mls. of solution (2) was added 10 mls. of triethanol amine, 10 mls. of ammonia-ammonia chloride buffer solution and 5 drops of eriochrome black T indicator. Titrated the solution against .01M, EDTA and the percentage of MgO present in the sample was calculated.

(f) Determination of Alkalies.

From the solution (2) the alkali metals were determined by flame photometery.

(xvii) Base Exchange Capacity:

A small known quantity of clay powder (-120 ASTM) was saturated with normal CH_3COONH_4. The mixture was shaken and few drops of NH_4Cl added to it as tracer. The clay was washed with CH_3OH of pH 7 till the excess of ammonium salts were freed. 2 c.c. of 50% NaOH solution was added to the washed clay, and ammonia distilled off. The distillate was collected in 2 c.c. of boric acid solution containing bromocresol green and methyl red and titrated with H_2SO_4. Millilitres of 0.1N H_2SO_4 used per 10 gms of sample would give meq of NH_4 per 100 gms. of clay or its base exchange capacity.

2.1.2 Fired Properties

The firing characteristics namely density, porosity and shrinkage of clays were determined, using a muffle furnace, in the temperature range of 600 to 1100°C employing three hours soaking period.

(i) Apparent Density:

A test sample (1" cube) prepared from the plastic mass and dried at 110°C for 2 hours was weighed (W_1) in air. It was immersed in kerosine oil for 24 hours to ensure the diffusion of oil into the pores and the oil saturated sample reweighed (W_2) in air. The difference ($W_2 - W_1$) was recorded to give the weight of oil diffused. The sample was finally weighed (W_3) in oil to get ($W_2 - W_3$) the loss of weight in oil. Apparent density was calculated as $W_1/(W_2 - W_3)xD$. Where D is the density of the oil used.

(ii) Apparent Porosity:

The liquid impregnation method as described above was employed to determine apparent porosity, using the equation:

$$P_A = \frac{(W_2-W_1)}{(W_2-W_3)} \times D$$

(Notations have their usual meanings).

(iii) Linear Shrinkage:

Two parallel lines were drawn on the face of the tablet prepared from the plastic mass and dried at 110°C. The change in distance between the lines were determined at various temperatures, multiple of hundred and the percentage shrinkage calculated at each stage. Average shrinkage of three specimens of each clay was recorded.

2.2 MINERALOGICAL PROPERTIES:

The section describes the experimental methods adopted to determine the mineralogical composition of clays using dehydration, differential thermal, x-ray and infrared analysis techniques.

(i) Dehydration Analysis:

One gram of clay (-120 ASTM) was heated in a platinum crucible at 100°C until no loss in weight occur. The percentage loss in weight was calculated and the process repeated at each step multiple of 100°C upto 1000°C. All weights were recorded, while the sample was hot. The heating rate of the furnace used was 10°C per minute. Loss in weight was plotted against temperature for each clay.

(ii) Differential Thermal Analysis:

D.T.A. was carried out on sample (-120 ASTM) using an automatic Hungarian derivatograph,

Type OD-102, with platinum sample holders and platinum-rhodium thermocouples. Heating rate employed during experiment was 10°C minute. Weight of each sample taken with the corresponding sensitivity was :

Clay No.	Wt. of the Sample	Sensitivity
Cl-1	1.8 gms	500
Cl-2	1.7 gms	200
Cl-3	2.0 gms	200
Cl-4	1.7 gms	200
Cl-5	1.1 gms	200
Cl-6	1.0 gms	100

In view of the variation in sensitivity and weights used, the amplification or e.m.f. in each thermogram was reduced to a uniform standard before interpreting the individual curves.

(iii) X-Ray Analysis:

X-ray analysis of clays (-300 ASTM) was carried out by X-ray diffraction method using 57.3 cms. Debye-Scherer Camera and Cu Kα radiations. The generator was run at 30 KV and 10 MA for different exposure periods, depending upon the crystallinity of each sample. All x-ray patterns were taken at about 30°C.

(iv) Infrared Analysis:

Infrared absorption spectra of clays were obtained (N.C.L. Poona) between 2-15 micron

using Nujol as mulling agent.

2.3 ELECTRICAL PROPERTIES:

Electrical properties of clays were determined, while adopting the following procedures.

2.3.1 Preparation of Clay Compacts

To the clay sample (-120 ASTM) dried to 110°C for four hours, was added 5 to 8% of water, depending upon the nature of the sample, for granulation. Granulated material was then passed through 40 and 80 sieves and (-40, +80) fraction used for preparing the specimens. Circular pellets (20 mm dia. and 2.5 mm thickness) were dry pressed at 5000 psi and dried at 110°C for about 24 hours.

2.3.2 Firing and Metallising

Clay pellets were fired in the temperature range of 800 to 1000°C employing 1,2 and 3 hours soaking period in a tube furnace using Platinum Rhodium thermocouple. The flat surfaces of the pellets were metallised by coating thin layer of silver paint and fired to 700°C for 10 minutes to get uniform deposition of the film.

2.3.3 Determination of Electrical Properties

Electrical properties, e.g.; electrical conductivity, dielectric constant, dielectric loss and dielectric strength of clay compacts were determined

following the procedures given below:

(i) Electrical Conductivity:

A constant potential of 500 volts from a power supply was applied across the pellet and the corresponding current flowing through it noted. The resistance was calculated using Ohms law. Actual resistance was determined by multiplying the observed resistance with a correction factor K, calculated for each sample; K being equal to $\pi d^2 / 4t$; where d, is the mean diameter and t, the thickness of the sample in cms. The reciprocal of the actual resistance was recorded as the conductivity of the specimen.

(ii) Dielectric Constant:

The capacitance of each specimen was determined at 1 MHZ with current magnification meter of type TF-1245, (Marconi Instruments Ltd. England) using the relation $C = C_1 - C_2$; where C_2 and C_1, represent capacitance with and without introducing the specimen.

The Q values corresponding to capacitances C_1 and C_2 were also noted and dissipation factor calculated as

$$\text{Tan}\,\delta = \frac{Q_1 - Q_2}{Q_1 Q_2} \quad \frac{C_1}{C_1 - C_2}$$

The dielectric constant (E) was calculated

using the relation $E = \frac{C.t}{0.0885\ A}$, where A is the area in cms^2; t, the thickness of specimen in cms and C, the capacitance in PF.

(iii) Dielectric Loss:

Product of the dielectric constant of the specimen and its dissipation factor ($E \times \tan\delta$) was recorded as dielectric loss.

(iv) Dielectric Strength:

In order to determine dielectric strength, two spots of 1 mm dia were made at the centre of the flat surfaces of the fired pellet with silver paint and fired to 700°C for 10 minutes. A varying potential from power supply of 5 KV range was applied across the pellet till it produced the spark. The voltage per mm thickness of the specimen was calculated to give its dielectric strength.

All the above properties were determined using three specimens for each clay and the average of their values recorded.

CHAPTER- III

OBSERVATIONS AND DISCUSSIONS

In this chapter, the results obtained on physico-chemical, mineralogical and electrical properties of clays have been discussed in details in sections 3.1, 3.2 and 3.3, respectively.

3.1 PHYSICO-CHEMICAL PROPERTIES:

Physico-chemical properties of clays are those qualities and responses which arise out of the mutual spacial relationship of its constituents. Over all observable properties both in raw and fired states are indeed a resultant of combination of physical, physical-chemical and chemical properties, each to a greater or lesser degree. The various physico-chemical properties studied have been divided into two parts, namely General and Fired and discussed in sub-sections 3.1.1 and 3.1.2, respectively.

3.1.1 General Properties

(i) Colour:

Colour is a manifestation of light energy and involves radiations of characteristic wavelengths, sensitive to the retina of a human eye. Though, apparently only a minor property in raw ceramic materials, colour indicates the presence of impurities in fired, as well as, finished products. It also contributes to beauty particularly in ornamental and some times in utilitarian-ware, where a desirable colour is required.

Observations (Table-1) show that Cl-1 and 6 are nearly white, while Cl-2 to 5 appear light grey. Colour of Cl-5, however, appeared more intense than Cl-2,3 and 4, as the latter samples have higher content of fine sand which decreases their colour intensity due to absorption phenomena. Colour of the clays, however, suggest the presence of varying amounts of carbonaceous matter, besides the compounds of iron and titanium, the chief colouring agents.

(ii) Texture:

Texture of a clay is said to be fine when its constituent particles are small and tightly packed. Coarse texture represents large and loosly spaced particles. Also, the shape and grading of the constituent grains determine this property. Texture affects significantly the plastic and fired properties of a material. Indeed, in the product of clay articles, an adequate understanding and appreciation of this property is very essential.

The texture of Cl-1 and 6 is observed to be extremely fine and that of Cl-2 most coarse. While the former two clays are composed of fine and closely packed particles as also they have higher density, the latter is most porous, light in weight and sandy in nature. Also, Cl-2 to 5 shrink rather slowly, as compared to Cl-1

TABLE - 1

General Properties of Clays

S.No.	Properties	Cl-1	Cl-2	Cl-3	Cl-4	Cl-5	Cl-6
1.	Colour at 30°C	White	Very Light Grey	Pearl White with Grey tint	Light Grey	Light Grey	White with Grey tint
2.	pH	8.40	7.90	7.80	7.85	7.50	7.80
3.	Slaking Time	24.7"	46.3"	1'-34"	2'-19"	3'-22"	11'-28"
4.	Swelling (C.C./gm)	1.16	0.05	0.25	0.20	0.40	0.15
5.	Water of Plasticity						
	Max.%	45.73	31.76	33.27	34.00	36.57	33.70
	Min.%	32.60	20.73	21.16	21.78	23.17	19.82
6.	Workability	Best	Very Poor	Fair	Fair	Poor	Best
7.	B.E.C.(meq/100 gm)	36.15	6.25	4.12	6.47	22.97	2.77
8.	Dry Linear Shrinkage (%)	15.20	1.50	3.70	5.00	10.20	4.50
9.	Dry Strength(lbs/inch^2)	380	79	122	180	350	230
10.	Heat of Wetting (cals/gm)	4.1	2.8	2.3	3.1	2.8	2.6
11.	Specific Conductivity (x 10^{-4} mhos)	1.298	0.628	0.636	1.098	1.250	0.416
12.	Spalling Resistance	Cracks appeared after 4-5 cycles	No crack appeared in 10 cycles				Crack appeared in Ist cycle
13.	Specific Gravity	2.32	2.22	2.30	2.25	2.20	2.69

and 6 as the former being coarser provide lesser surface area of contact between its constituent particles than the latter. Lesser the area of contact between the adjacent particles, slower will be the reaction and higher the temperature at which shrinkage takes place.

(iii) pH:

Most of the natural clays contain hydrogen, in part at least, as their exchangeable cation. It is, because clay particles have a tendency to absorb hydrogen ions preferentially. Consequently, when a clay is suspended in water, dissociation takes place and hydrogen ion concentration in the suspension increases. Since this concentration is extremely small, it is generally expressed as the logaritham of its reciprocal known as pH. The pH of pure water which contains 10^{-7} gram of ions per litre is taken as 7. Solutions having pH less than this are acidic, while those with higher values are alkaline in nature.

The pH of clays (Table-1) lie in the range of 7.5 to 8.4 at room temperature ($30^{o}C$), indicating their alkaline nature, though the alkalinity varies in each case. Cl-1 and 2 are more alkaline than Cl-3,4 and 6, all of which show roughly the same value. Cl-5 is least alkaline.

(iv) Slaking:

When a lump of clay is immersed in sufficient

amount of water, the electrostatic forces, binding its constituent particles get weakened[187] and eventually it becomes a soft 'mushy' mass. This physical change which is known as 'slaking' has important practical significance in ceramic industry, where the raw materials have to be converted to a slip or plastic mass for moulding and shaping purposes. Clays which slake fast can easily be tempered or mixed to form a homogenous mass.

Slaking tests (Table-1) reveal that Cl-6 takes maximum time to disintegrate completely followed by Cl-5. Rest of the samples slake in less than 2'-18". The variation in the slaking time can be attributed to the porosity, as well as, the forces of cohesion between the particles constituting the individual sample. Cl-2 which is most lean and porous slakes much faster than other clays. Being sandy in nature and stabilis-ed by only water film, it appears to collapse merely under gravitational force without any appreciable swelling. The minimum time taken by Cl-1 for disintegration is compatible with its maximum swelling, reflecting the development of internal stresses in its fabric. With absorption of water, the absorbed films are enlarged causing decrease in cohesion between the particles resulting in its faster slaking. Cl-6 slakes very slow as it is most hard and dense with practically non-swelling character.

(v) Swelling:

When a piece of clay is submerged in water, the latter gradually permeates through the former, loosening and separating its constituent particles and resulting in an increase in its volume. This phenomena which is known as swelling is due to the absorption of water within the crystal lattice. Swelling behaviour of a clay sample depends upon various factors, e.g., (a) the type and amount of clay mineral present in it, (b) the nature and amount of exchangeable ions associated with it, (c) the shape and the size of its constituent particles and (d) the nature of soluble salts present in it.

Swelling behaviour of clays (Table-1) indicate that Cl-1 shows maximum swelling of 1.16 c.c/gm. followed by Cl-5,3,4,6 and 2. The observed swelling behaviour of clays is fairly compatible with their texture, plasticity, base exchange capacity, chemical and mineralogical composition. Cl-1 besides being most plastic and fine in texture also shows higher bec and montmorillonite content in it. Clays which swell more show higher plasticity and bec. Mering[188] has suggested that in montmorillonites the absorbed water is associated with exchangeable base where the water molecules coordinate around cations between the layers of this mineral. Calcium bearing

montmorillonites, unlike sodium based, absorb less water and thus do not show progressive hydration resulting in low swelling as observed in Cl-1 to 5. Least swelling of Cl-2 is also because of its much coarser and sandy nature. Cl-6, though fine in texture, is kaolinitic sample with very low bec and least amount of soluble salts and hence shows poor swelling character. Swelling of clays is fairly compatible with the calcium-magnesium oxide content in them.

(vi) Dry Linear Shrinkage:

It is defined as the reduction in size, measured in length, when pore water is driven off from a clay mass. It has been suggested[192] that with the removal of pore water, clay particles tend to take up positions within the force net work such that in new stable position they have minimum energy. Such a movement of particles usually accompanies plastic deformation.

Dry linear shrinkage of Cl-1 (Table-1) is highest followed by Cl-5. Cl-2 and 3 shrink least. In general, dry linear shrinkage is directly related[193] to the water of plasticity. Also, finer the particle size, finer will be the capillary pore system in it and greater will be the amount of water retained, as compared to a sandy clay, where particles are larger, round in shape and material has high porosity. High value of dry linear shrinkage of Cl-1 and 5 may be attributed to the higher

content of water in them, their finer particle size and higher plasticity. Low values observed in Cl-2 and 3 are due to low water content, besides their coarser nature. Also, their poor structure and presence of non-clayey material in them decreases their shrinkage. Low value of Cl-6, which though very fine in texture, is attributed to its very low interlayer water content and kaolinitic character[194,195] with quartz as a constituent mineral. Dry linear shrinkage of clays bears direct relationship with their data on water of plasticity.

(vii) Dry Strength :

Determination of the hardness of raw clays is indeed important in so far as it is related to the preparation of clays for use in industry is concerned. It is because clays are usually crushed grounded and converted into plastic mass or slip before moulding. Clays which can easily be crushed to a fine size will be cheaper, easy to prepare and, therefore, more desirable than hard ones. In ceramic bodies which are largely composed of single mineral, the measurement of this property can prove reliable guide to their composition, although in composite bodies it has little significance. Indeed, dry hardness values of clays vary and do depend upon the history of the samples - the metamorphic changes undergone by them and the pressures to which they have

been subjected, besides their mode of formation and location etc. Literature[189,190] provides wide range in the dry strength values of individual clay minerals, depending upon the variation in particle size distribution, degree of crystallinity and the nature of the associated exchangeable ions. Dry strength of montmorillonite and illite is, generally, higher than kaolinite. Poorly crystalline minerals show higher dry strength as compared to well organised minerals. Likewise, a clay composed of mixed layer assemblages will give higher strength than that with similar composition but with components present in discrete units. Further, high dry strength is exhibited by clays composed of fine particles with higher density and uniform texture. It is believed[22,23,191] that Na^{+}, if associated, add to the dry strength more than Ca^{++} or Mg^{++}. Presence of vegetable material acts as gluing or cementing material and also enhances dry strength. Thus none of the factors, as discussed above, can solely determine this property.

Observations on dry strength of clays (Table -1) indicate that Cl-1 exhibit maximum strength followed by Cl-5, it is least in Cl-2. Highest strength attained by Cl-1 and 5 may be attributed to their fine particle size distribution. Also the montmorillonite content in them is maximum which contribute to their higher

strength due to better interlocking of constituent particles. Although Cl-2 and 3 contain maximum percentage content of sodium ions, yet their comparatively low strengths may be ascribed to coarser and highly sandy nature and proportionately lesser amount of montmorillonite content in them. With the exception of Cl-6, the strength of all clays bear a direct relationship with their plasticity data, Cl-6 though very fine and highly plastic clay, yet gives low strength possibly due to the presence of kaolinite and quartz, both of which contribute to higher porosity and provide a very weak bond resulting in decrease in the strength. Thus the texture of the clay alone does not seem to be adequate enough to determine its strength. Too many fine particles can also cause excessive shrinkage, warping and distortion and reduce the strength.

(viii) Plasticity:

Plasticity, in all its aspects, is an interguing phenomena in clay technology and may be defined as the behaviour of clays when they are mixed with insufficient amount of water to permit flow. Clay workers, often define it in terms of shortness or fatness, depending upon the feel of the material. Unlike viscosity where the suspension is sufficiently poor to flow under its own weight, plasticity represents the condition when the body can sustain its own weight, but can be made to flow only under applied pressures. As the water content of

suspension is reduced relative to the amount of the clay, the lubricating effect of the former decreases, causing a decrease in the separation between the individual clay particles and thus hindering free flow of the mass. In this situation, the resistance to shearing forces increases and when it is sufficiently large, the change in shape of the mass becomes permanent. Plastic flow implies that certain yield values must be exceeded before any deformation takes place. Further, unlike viscous flow, it is irreversible phenomena. Plastic flow does not occur until the force reaches certain minimum value and when the force is removed, the shape of the plastic body becomes permanent and does not return to its original shape. Of course, there is no sharp dividing line between the viscous and plastic flow but the gradual transition from former to the latter takes place as the amount of liquid medium is decreased.

In order to explain this property, it is believed that clay particles when suspended in water are surrounded by hydrospheres which contain ions of different charges. Around the ultimate particle there is a layer of negatively charged ions which are balanced by the sphere of cations diffusing into the hydrosphere. When the hydrosphere is large, the particles in the suspension are free and viscous flow results. If the

hydrosphere is small, the water films separating the particles become thin resulting in greater cohesion between them. The counter cations provide link between particles and rigidity in linkage results in plasticity. Under the applied pressure, charged particles move and equally stable system is formed simultaneously, which retain its shape even after the removal of the force. Thus, plasticity is associated with thin water film around the individual particle. If the thickness of the film is more than required, free flow will occur producing plasticity; but if it is less, the individual particles will touch each other and the plasticity will be destroyed. Indeed, plasticity is a function of water content, the optimum value being dependent upon the surface area capable of being wetted. The absorbed water film provides the continum in the mass and introduces rigidity, as well as, the ease of deformation. It is believed[196] that in clay particles the thickness of the film is of the order of 2000 ^{0}A units.

Water of plasticity depends upon many other factors[197-201] also, such as shape, size orientation and surface area of particles, besides the previous history of the individual sample.

Observations show that Cl-1 (Table-1) is highly plastic followed by Cl-5 giving 45.7 and 36.5 percent of maximum water of plasticity, respectively.

Rest of the clays are roughly equally plastic, except Cl-2 which is least. It is believed that clays which swell more also give higher amount of water of plasticity. Although, no exact relationship could be established between the two, yet the overall observations of plasticity are fairly in agreement with the swelling behaviour of clays. Observations on minimum water of plasticity also places Cl-1 as highly plastic and Cl-2 least.

Atterberg[202] expressed the plastic properties in terms of plastic limit, liquid limit and plasticity index etc. which have been described[203] and defined[204] as :

(a) Liquid Limit.

The moisture content (percent by weight) of oven dried soil at which it just begins to flow when slightly jarred.

(b) Plastic Limit.

The minimum moisture content (percent by weight) of oven dried soil at which it can be rolled into threads of 1/8" dia, without breaking into pieces.

(c) Plasticity Index.

The difference between the liquid limit and plastic limit defining the range of moisture content in which the soil remains plastic.

Various plastic flow characteristics such

TABLE - 2

Plastic Flow Characteristics

Characteristics	Cl-1	Cl-2	Cl-3	Cl-4	Cl-5	Cl-6
Liquid Limit	50.80	36.20	34.20	34.30	41.20	30.40
Flow Index	8.40	3.85	5.00	5.00	4.20	5.20
Plasticity Index	16.20	16.70	9.50	14.30	18.90	15.00
Toughness Index	1.92	4.39	1.90	2.86	4.50	2.88
Liquidity Index	- 1.20	- 0.88	- 2.06	- 0.92	- 0.72	- 0.94
Consistancy Index	2.20	1.88	3.06	1.87	1.72	1.94

as, liquidity limit, flow index, plasticity index, toughness index and consistancy index, as determined by Atterberg apparatus are given in Table-2. The order of the liquid limit is the same as the water of plasticity determined by adding water, drop by drop, to the clay powder. Small variations in the values may be due to the personal error involved in the finger print method.

(ix) Workability:

Workability is associated with a high yield point and a large plastic deformation. Workable materials must have particles which hold themselves together strongly and allow a large relative sliding movement without rupturing the bonding medium. Such conditions are generally satisfied by small particles, although the type of minerals present in a material also influence this property according to the extent to which they fulfil the required conditions[35].

Observations on workability (Table-1) indicate that Cl-1 and 6 are most satisfactory as compared to Cl-3 and 4. Cl-2 is found to be very poor to work with perhaps because of its highly sandy nature. Workability of clays do not seem to show any cognizable relationship either with water of plasticity or particle size. Cl-6 though having low percentage of water of plasticity is yet very good to work at as compared to Cl-5 with higher percentage of water of plasticity. Similarly Cl-1 and 5

though are roughly equally fine, yet Cl-5 is comparatively very poor to work with. It is believed that besides the fineness of the particle, presence of vegetable or organic materials and the chemical composition of clays are important factors which may govern the workability of a clay. For example, calcium based clays are very good to work at irrespect of their particle size. Similarly, clays having vegetable or organic materials are also very satisfactory from workability point of view. Workability of Cl-1 and 6 may be assigned to any of these factors.

(x) Viscosity:

Viscosity of a liquid indicates its ease to flow and may be defined as the ratio between the force or stress applied to a liquid and the shearing strain or the rate at which the fluid resists to change its shape or motion. It is the frictional resistance of the molecules of the liquid which is offered to similar molecules in their immediate vicinity. In an ideal liquid the flow is Newtonian i.e. the ratio of stress to strain is constant and independent of the applied force. When the concentration of the suspension is increased and clay minerals are added, the deviation from the Newtonian flow occurs and the rate of flow induced in the suspension would depend on the resistance of the molecules of the medium and the concentration of particles in it. Philipp-of[205] has

suggested that viscosity of a suspended medium also depends upon the size and shape of the particles; the type and concentration of the electrolytes used; the temperature of suspension etc. For very low concentration of the particles when their electric fields do not interfere, Einsteins equation holds true[41, 206]. The concentration at which the particles are so close that free rotation is not possible has been defined[207] as critical point. Further, the viscosity of a given slip concentration increases as the size of the particles decrease. Plate like fibrous particles with surface factor larger than cubic or spherical particles increase the viscosity.

Viscosity observations at room temperature (Fig. 1) show Cl-1,5 and 6 more viscous than rest of the samples due to their finer particle size. With the increase in concentration, as expected, clay particles become progressively close to each other thus increasing the frictional resistances and reducing the free motion of the fluid, hence increasing the viscosity. At 0.10 gm/ml. concentration of suspension, the increase in viscosity is found to lie between 19-29%. The high viscosity of Cl-1,5 and 6 can also be explained on the basis that the hydrospheres surrounding the particles of these clays are weakly held and get distorted easily than those of other clays which seem to be more rigidly held.

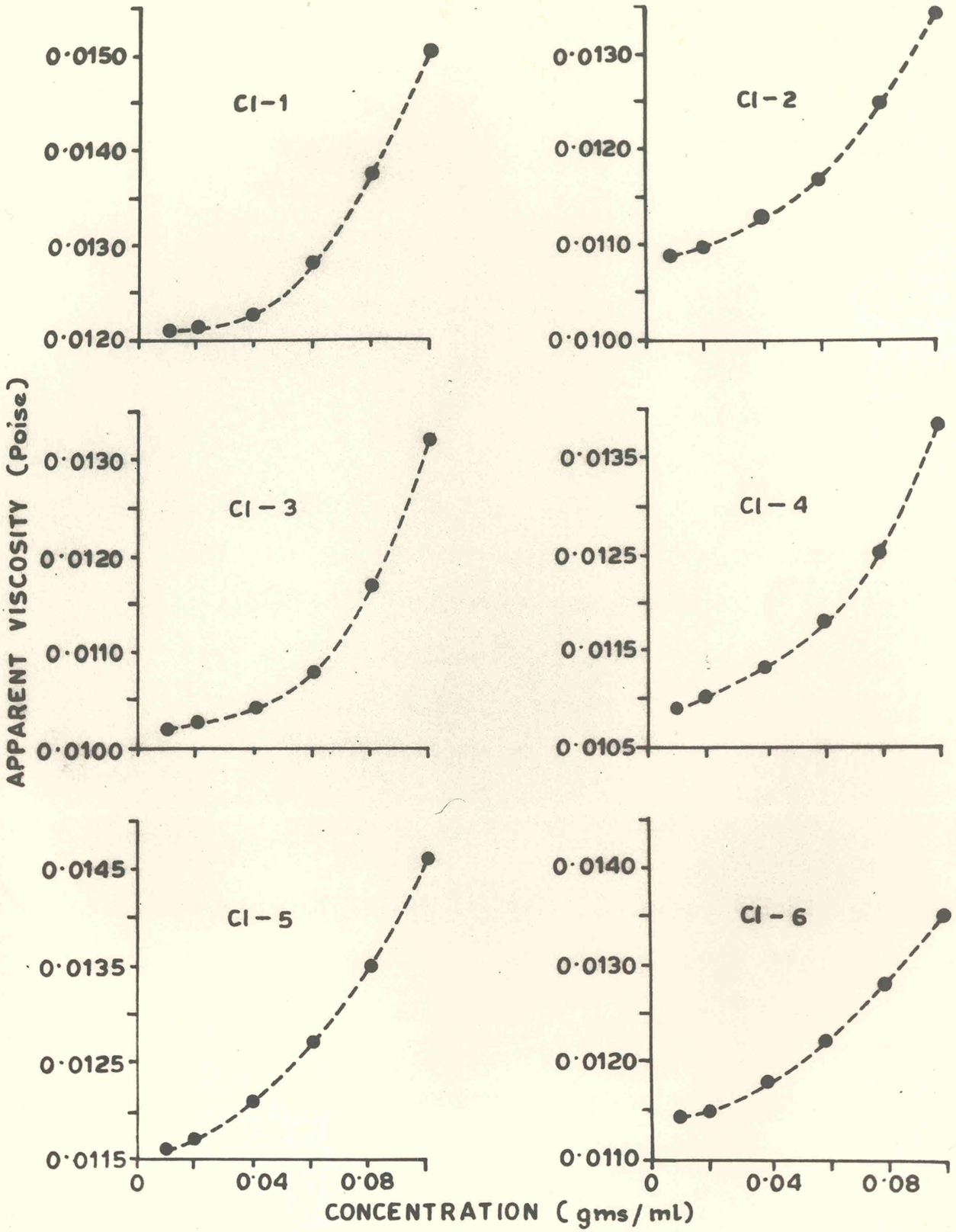

FIG.1. EFFECT OF THE CONCENTRATION OF CLAY SUSPENSION ON THE APPARENT VISCOSITY.

The effect of the addition of electrolytes e.g. sodium carbonate and sodium silicate on the viscosity of 5% clay suspension has also been studied and plotted in Fig. 2. It is observed that viscosity decreases by 14-20% and 23-33% corresponding to the addition of 4 meq of sodium carbonate and sodium silicate, respectively. Beyond this critical point, the separation distance between particles becomes less than the size of particles in the suspension with the result that the curve maintains constancy even with further addition of electrolytes. Observe decrease in the viscosity is due to the decrease in surface tension of particles in the medium, as the addition of electrolytes reduce the drag[44] of the particles in water. Norton[208] has suggested that in floculated system, the individual particles are in equilibrium position, with respect to each other, on account of the forces of attraction and repulsion. Flow in this condition is possible only if the applied force disturbs the equilibrium. In defloculated system, however, the attractive forces between the particles are absent resulting in much greater viscosity with even slight disturbance.

(xi) Particle Size Analysis:

A natural occuring clay is, generally, composed up of particles of different sizes, ranging from below 1 to 20 micron and even above. Strictly speaking,

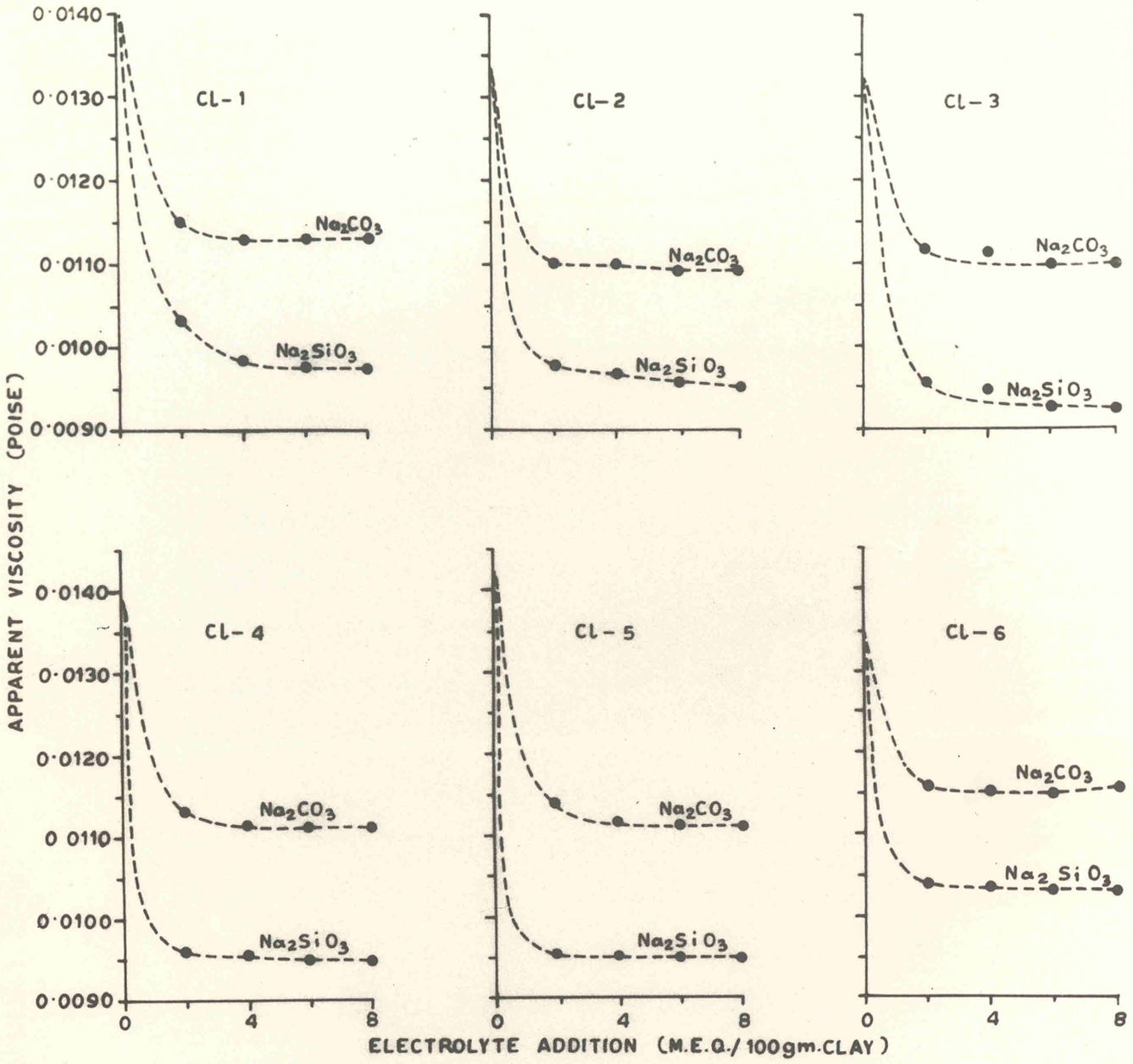

FIG. 2. EFFECT OF SODIUM CARBONATE AND SODIUM SILICATE ON THE APPARENT VISCOSITY OF CLAY SUSPENSION.

the size of a clay particle lies below 2 micron and coarser particles are considered silt and sand fractions. In a clay based industry classification of the particle size and the separation of its various fractions has wide implications, if the product is to satisfy certain specifications, particularly with regard to its texture, density and porosity. Such a classification and separation indeed attains importance when oversized and undersized undesirable particles are to be removed from the material or conversely, separated out valuable fine or coarse ingredients. As the raw material is composed of grains of various shapes and sizes, particle size distribution implies either the size of inherent mineral crystallite, which is extremely small; or grain size distribution. This property, although, very important from industrial point of view, is yet difficult to determine accurately because of innumerable inherent difficulties.

The particle size analysis of clays (Fig.3) indicate that Cl-6 has about 47% of the particles below 5 micron followed by Cl-5 with nearly 35%. The percentage of this size is least in Cl-2 with only 13%. Further, it is revealed that Cl-6 contains about 33% particles between 5 to 20 microns whereas in other clays except Cl-2, this percentage varies between 40-45%. The presence of very high percentage of coarser particles in Cl-2 indicate that

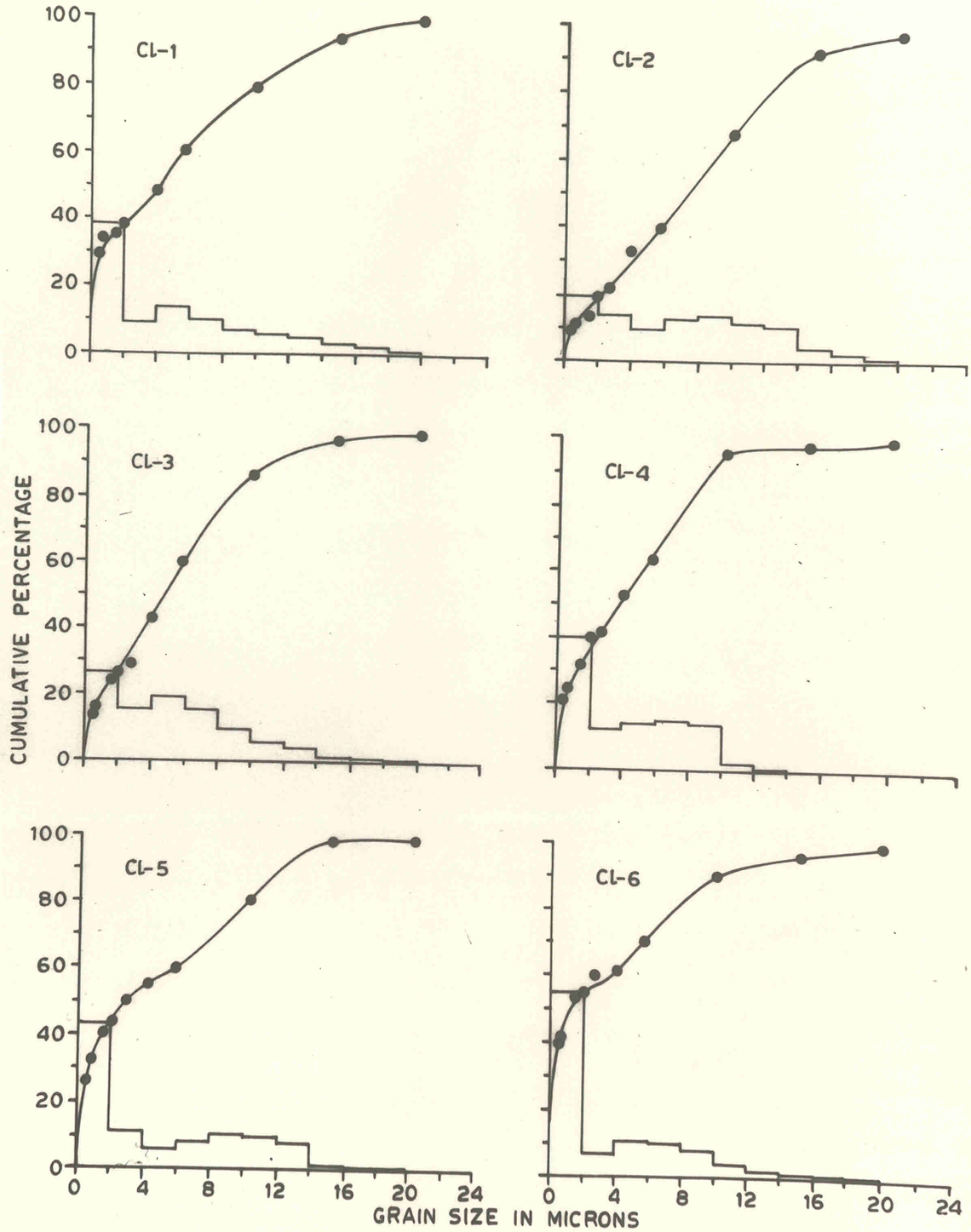

FIG. 3 HISTROGRAMS SHOWING THE GRAIN SIZE DISTRIBUTION IN CLAYS.

it has some non clayey material in it. Cl-2 is highly silicious in nature as revealed by chemical analysis, density, porosity and shrinkage data. The particle size analysis of Cl-1,3,4 and 5 is comparable to bentonites of rather poor commercial quality.

(xii) Mechanical Analysis:

Mechanical analysis of clays (Table -3) supplements particle size analysis data reveals that Cl-1 and 6 contain much higher percentage of fine particles than Cl-2 and 3. Although, the plasticity of a clay is not an index of particle size distribution in it yet the minimum plasticity of Cl-2 may be attributed to its coarser nature and much higher plasticity of Cl-1,5 and 6 to higher percentage of finer particles in them.

(xiii) Specific Gravity:

The true specific gravity of a substance is defined as the ratio between its weight and that of an equal volume of water. In case of crystals, it may be expressed in terms of the dimensions of atoms or ions in the lattice. The weight of an atom or ion and the way in which they are arranged greatly influence the specific gravity of the samples. Ceramic materials, which are composed of many crystals and perhaps even colloidal or glassy substances; the specific gravity would be determined as the resultant of the different components present.

TABLE - 3

Mechanical Analysis of Clays

Constituents	Cl-1	Cl-2	Cl-3	Cl-4	Cl-5	Cl-6
Clay .001-.002 mm	9.1 %	3.7 %	3.1 %	10.9 %	20.1 %	24.9 %
Very Fine Silt .002-.005 mm	9.2 %	11.6 %	8.2 %	5.2 %	7.8 %	12.4 %
Fine Silt .005-.01 mm	12.2 %	7.8 %	16.8 %	10.1 %	20.7 %	15.2 %
Silt .01-.02 mm	8.4 %	18.9 %	16.3 %	9.7 %	9.4 %	7.4 %
Very Fine Sand .02-.05 mm	5.3 %	13.7 %	12.6 %	3.3 %	0.3 %	0.9 %
Sand Particles larger than .05 mm	31.2 %	38.2 %	32.6 %	47.4 %	32.4 %	32.3 %

(Percentages exclude L.O.I.)

Specific gravity of clays (Table-1) lies in the range of 2.20 to 2.32 except Cl-6, which gives comparatively higher value. Cl-2, however, shows the least, possibly due to the presence of higher silica content in it. Higher specific gravity of Cl-6 may be attributed to its kaolinitic character besides the presence of quartz in it. The individual atoms in the quartz lattice are arranged in such a way that its packing is believed to be very close, resulting in an increase in the specific gravity. The variations observed in the specific gravity values of Cl-1 to 5 may be due to the fact that they contain varying amount of water as an integral part of their structure.

(xiv) Specific Conductivity:

Clay suspensions and particularly slips possess electrical properties which are important in connection with the purification of the materials and also in production by castings. While the electrical conductivity of pure distilled water is of the order of 10^{-6} mhos at $18^{\circ}C$, the presence of minor quantities of soluble salts can cause a marked difference in its value. Clays when suspended in water conduct current, primarily depending upon the nature of the colloidal material present in them and its tendency to ionise.

The specific conductivity data of the samples (Table-1) indicate that Cl-1 gives highest specific

conductivity of 1.298×10^{-4} followed by Cl-5 which gives 1.250×10^{-4} mhos/cm. The specific conductivity of Cl-6 is found to be least. Higher values of Cl-1 and 5 can be attributed to higher amounts of soluble salts present in them. Cl-6 with minimum capacity of conducting current also swells least. The general range of specific conductivity observed in these clays appear to be related to their swelling behaviour and fairly in agreement with the values reported[209] for similar type of clays.

(xv) Heat of Wetting:

When a dry clay is mixed with water, alcohal or certain other organic liquids, a rise in temperature of the latter is observed as a consequence of the heat evolved by the former. The heat so evolved is known as the heat of wetting or Pouillets effect. Although, different causes of heat of wetting have been reasoned out by various workers[37,79,210], yet it has been generally agreed upon that a change in state of water which is directly adjacent to the adsorbing surface and the possible hydration of adsorbed ions, are the basic reasons culminating to this phenomena. Furthermore, it has also been suggested[211,212] that montmorillonites owing to higher cation exchange capacity yield higher values for heat of wetting, whereas kaolinites for the same reason, give low values. However, increase in particle size increases heat of wetting in kaolinites[75].

Observations on the heat of wetting (Table-1) indicate that it is highest in Cl-1, while in other clays it is low and varies from 2.3 to 3.0 cals/gm. High value of heat of wetting of Cl-1 may be attributed to its higher bec and also its finer particle size. In general, the results on heat of wetting of clays appear compatible with their bec and particle size observations. Since the nature of adsorbed cations also influence this property, no exact linear relationship could be established between heat of wetting and bec.

(xvi) Spalling Resistance:

Many ceramic materials are unable to withstand sudden changes in temperature without disintegrating in one form or the other. The ability of a material to resist such a treatment is known as thermal shock resistance, which is manifested in the form of cracking or spalling, as a consequence of internal stresses developed during heating or cooling. It is believed that in the absence of controlled heating, thermal gradients set up between the adjacent areas of the body, giving rise to stresses, which if exceed the elastic limits of the body will cause spalling. Besides controlled heating, the size and shape of the body, the texture of the material and even the nature of surrounding medium to which heat is radiated out, affects this property greatly.

Spalling resistance tests (Table-1) indicate that cracks do not appear in Cl-2,3,4 and 5 even upto 10 cycles of operation, whereas in Cl-1 and 6, they are initiated in 4 and 1 cycle, respectively. These results can be explained on the basis of the fineness of these samples. Since, Cl-6 is the finest clay followed by Cl-1, they offer very low resistance to thermal shocks. Cl-2 to 5 are comparatively coarser clays and, therefore, show greater resistance.

(xvii) Chemical Analysis:

Chemical analysis of clays is given in Table-4. Although, it is difficult to properly identify the constituent minerals present in each sample only on the basis of chemical analysis data, yet it is possible to categorise Cl-1 to 5 akin to bentonites on the basis of their SiO_2/Al_2O_3 ratio. Cl-6 appears to be kaolinitic in character. It has been suggested[12,213] that chemical analysis of bentonites widely vary due to the wide range of substitution within the lattice and also due to the variation in nature and amount of exchangeable ions. Thus silica-alumina or silica-sesquioxide ratio cannot be taken as dependable criteria to identify correctly clay mineral constituents.

Cl-1 shows higher loss on ignition than rest of the samples. Although, it is generally considered

TABLE - 4

Chemical Analysis of Clays

Constituents	Cl-1	Cl-2	Cl-3	Cl-4	Cl-5	Cl-6
SiO_2 %	48.56	67.25	59.60	64.60	59.65	59.20
Al_2O_3 %	20.89	15.20	18.62	19.50	17.80	29.35
Fe_2O_3 %	1.10	2.07	3.22	1.17	3.97	1.42
TiO_2 %	0.16	0.28	0.40	0.15	0.15	1.07
CaO %	3.00	1.96	2.30	1.59	2.51	1.45
MgO %	4.27	1.94	2.80	1.83	2.82	1.00
Na_2O %	0.53	3.47	2.72	0.24	0.35	0.15
K_2O %	0.28	1.84	1.91	0.12	0.18	-
L.O.I. %	21.61	6.67	9.96	9.15	12.00	6.08

that the presence of organic or vegetable material increases this loss, yet in case of Cl-1, the presence of higher percentage of hydrates of Ca^{++} and Mg^{++} and low content of Na^{+} and K^{+}, appear to be more important factors for its high loss on ignition. Comparatively low loss on ignition of Cl-2 and 3 in particular, is due to lower content of Ca^{++} and Mg^{++} and higher percentage of Na^{+} and K^{+} in them, besides their more silicious nature. Ca and Mg montmorillonites tend to be more highly hydrated than Na or K based.

While the percentage of iron content in Cl-5 is higher than rest of the clays, fluxing oxides other than those of silica and alumina vary between 5-12%.

(xviii) Base Exchange Capacity:

Clay minerals have the property of absorbing certain ions[214] and retain them in exchangeable state around silica-alumina structural units without effecting the structure of the latter. Montmorillonites and even fine grained illites show the capacity of absorbing cations due to charge deficiency within their lattice. These cations are held by weak electrical forces and can be easily replaced by others. Thus the absorption of charge in this way does not involve any structural change; one base is taken up from the solution, another is, generally,

released in its place. Since it is recognised that the exchange can take place between the cations, e.g.; NH^+_4 by Na^+, this property is appropriately named as cation exchange capacity. Customerily, a clay with sodium as absorbed cations is called as sodium-clay, whereas the one with calcium cations is referred as calcium clay. The exchange reaction between the cations associated with clay is usually expressed as :

$$(Clay)\ Na + NH_4OH \rightleftharpoons (Clay)\ NH_4 + NaOH$$

Ion exchange capacity has wide importance in many physical properties of clay minerals. Plasticity of a clay depends upon the type and amount of exchangeable cations it possesses. It is also possible to determine and change the plastic flow characteristics of many clays through base exchange reactions.

The base exchange capacity of clays (Table-1) shows that Cl-2 to 4 and 6 give comparatively much lower values as compared to Cl-1 and 5 due to low water of plasticity and higher percentage of sand in the former. Further, the swelling behaviour of these clays is also very poor suggesting the small percentage of exchangeable ions in them. Base exchange capacity observations indicate that except Cl-6, all samples are calcium-magnesium based clays, though containing small

amounts of alkali cations. The chemical and mineralogical analysis of Cl-1 to 5 also suggest their bentonitic character with different amounts of montmorillonite mineral; Cl-1 and 5 having comparatively higher content. Swelling behaviour and bec of Cl-1 and 5 also supplement these results. Since, Cl-6 is kaolinitic in nature and associated with quartz and illite, it gives lowest value of bec.

It has been shown that broken bonds around the edges of silica alumina units give rise to unbalanced charges which would be balanced only by absorbing cations. The number of broken bonds and hence the exchange capacity will increase as the particle size decreases. Johnson[215] argued that total exchange capacity of montmorillonite is mainly attributable to their broken bonds. Higher bec of Cl-1 and 5 may also be due to their smaller particle size as compared to other samples. Presence of quartz and illite, both of which give poor exchangeable capacity contribute towards very low bec of Cl-6.

3.1.2 Fired Properties

(i) Colour:

Although, there are many minerals and ceramic materials like alumina, silica, magnesia, lime, china clay, talc etc. which are perfectly white, yet the natural clay minerals are invariably impure and possess

different colours depending upon the type of impurity, its amount and state of sub-division etc. Also, the firing conditions, nature of the fluxes, presence of components which can modify the colour and the extent of vitrification of the samples often control the colour of the fired products.

Fired colour of samples (Table-5) indicate that Cl-1 develops ivory colour around 800°C getting darker with increase in temperature. Cl-2,3,4 and 5, however, first become pink, tending to buff around 1100°C. Cl-1, unlike Cl-2,3,4 and 5, maintain ivory colour from 800 to 1100°C, as it contains minimum amount of iron and titania, the two chief colouring agents. Cl-6 turns creamish yellow in this temperature range, due to highest percentage of titania in it. Dull appearance of Cl-1 and 6 at 1100°C indicate the possible presence of some humous material in them. Cl-2 becomes pink beyond 800°C due to the fact that it contains less percentage of iron and titania as compared to Cl-3 and 5 which become buff at this temperature. Cl-5 is dark buff as it contains highest percentage of iron. The least reflecting surface of Cl-2 at 1100°C may be attributed to the highest percentage of silica content in it, whereas the lustrous surfaces of Cl-3,4 and 5 may be due to the fusion of clay minerals into glassy matrix or the presence of some salts, which during heating migrate to the surface, rendering them shine.

TABLE - 5

Variation of Colour with Temperature

S.No.	600°C	700°C	800°C	900°C	1000°C	1100°C
Cl-1	White	-	Ivory	Ivory	Ivory	Ivory
Cl-2	Light Pink	Pink	Pink	Pearl	Buff	Buff
Cl-3	Light Pink	Pink	Pink	Pearl	Buff	Buff
Cl-4	Light Pink	Pink	Pink	Pink	Buff	Buff
Cl-5	Pink	Pearl	Oak	Oak	Dark Buff	Dark Buff
Cl-6	White with creamish tint	White with greenish tint	Creamish	Creamish	Creamish	Creamish Yellow

It is believed[216] that in ceramic materials, it is the presence of the elements of transition group which play significant role in imparting colour. Iron Copper and Cadmium etc. have unfilled 'd' shells and are capable of having variable valencies. The electrons in these shells can easily interchange their orbits when excited, imparting colour to the material. Nyburg[217], however, suggested that the ions of these elements are in complex coordination and the manner in which they are associated with the material will determine the colour.

(ii) Apparent Density:

Density which may be defined as mass per unit volume is yet another property which characterises a given material. There are various factors such as texture, structure, porosity, chemical, as well as, mineralogical composition, which control this property. Furthermore, the pressure and the heat treatment to which the material is subjected, also affects its density significantly. The variation in density at initial temperature, is due to the removal of loose water and has practically no importance. However, at elevated temperatures, the variation is owing to the melting of minerals. Even when only partial fusion occurs, the changes in density are often much more rapid than at slightly lower temperatures, and the product may be quite different in character, even though its composition

remains unchanged. At higher temperatures finely divided particles react much more readily than coarser ones[218], resulting in the formation of more dense mass. Also, the impurities present play an important part in changing density by combining with a portion of it to form a fusible material of different nature.

Density variation of clays with temperature between 600 to 1100°C is plotted in Fig.4. Observations reveal that the density remains practically constant between 600 to 800°C in all the samples, except Cl-6 in which the constancy period extends upto 900°C. This constancy period of the curves indicate that the hydroxyl loss and accompanied changes in dimensions in this region are such that they do not practically contribute towards any change in the density. Beyond constancy period, all clays show a gradual rise between 800 to 900°C, with the exception of Cl-6 in which case this period is extended by 100°C. After 900°C, the curves exhibit a steep rise upto 1100°C, due to the fluxing action of alkalies and other mineral impurities present in the samples. Maximum density of Cl-1 at 1100°C followed by Cl-5 is primarily due to their finer particle size. The minimum value of Cl-2, at both room and elevated temperatures, may be attributed to the presence of higher silica content in it. Comparatively, smaller and gradual rise of the density curve of Cl-6 upto 1000°C is

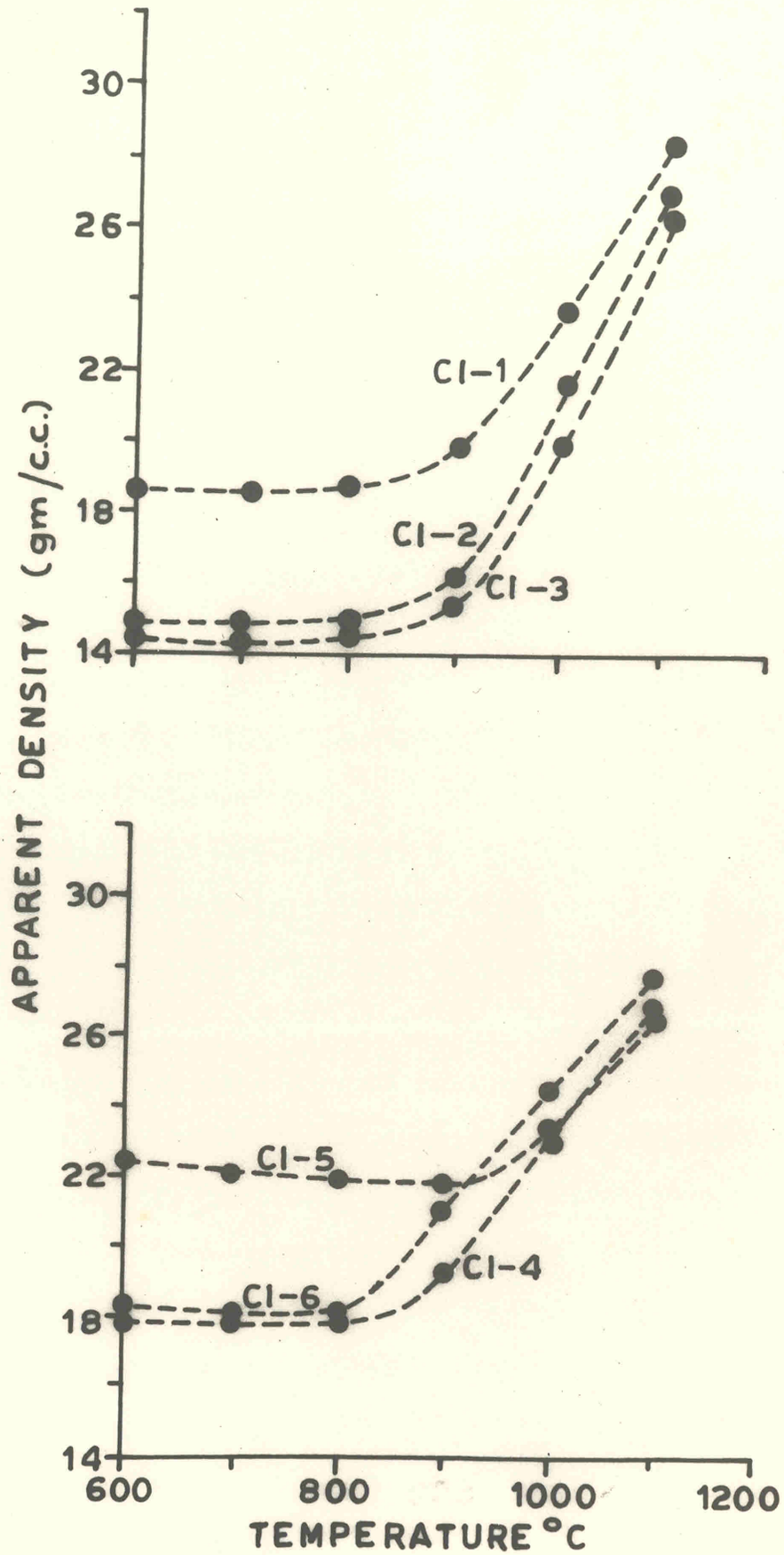

FIG. 4. TEMPERATURE VARIATION OF APPARENT DENSITY OF CLAYS.

due both to the presence of quartz and low amount of fluxes in it.

(iii) Apparent Porosity:

Ceramic raw materials, with the exception of some types of glasses, are porous and invariably contain a fraction of the total volume of the material composed of air, filled in the pores or voids. Pores exist in various types[219], such as; (a) Close or Sealed pores (b) Channels connecting separate pores (c) Blind-Alley pores (d) Loop pores (e) Pocket pores and (f) Micropores. Consequently, there are two types of porosities: True and Apparent. While True porosity is the ratio of the volume of all the pores and voids, both open and closed and the total volume of the body; the Apparent porosity is the ratio between the volume of water or liquid capable of being absorbed into it and the total volume of the body.

Porosity of an article depends upon the size, shape, grading and relative orientation of the particles, besides the nature of the material and the pretreatment to which it is subjected during manufacture.

In general, porosity of a mass increase if it contains components which volatalise, evaporate or decompose liberating gases. Thus, during drying, although the water is driven out from the pores resulting in minor re-arrangement in the disposition of the individual

particles, yet the water lost is entirely replaced by air. If the material contains carbonaceous or other organic matter, porosity increases due to oxidation or burning. Decomposition reactions with the liberation of gases or destruction of minerals and other hydrous substances, besides dissociation of carbonates, tend to enhance porosity around 800°C.

Materials which fuse or fluxes which combine with other mineral constituents to form a liquid, generally, decrease porosity. The extent of decrease, however, depends upon the type of fluxes; the form in which they are present; the grain size of the minerals which contain them and the temperature of firing. Alkalies form liquid with alumina and silica at much lower temperatures than other fluxes and are, therefore, more effective in reducing porosity.

Mixtures of fine particles have a large surface factor and are thus more porous in the raw state than those containing coarse particles. However, at high temperatures material with fine particles fuses much more easily than coarse grains resulting in decrease in porosity.

Temperature variation of porosity of clays (Fig.5) show that at 600°C their porosity lies between 24 to 30%. Slight increasing trend of curves between 600°C to 800/900°C indicate the presence of some carbonaceous material, as well as, their coarser nature. Maxima around

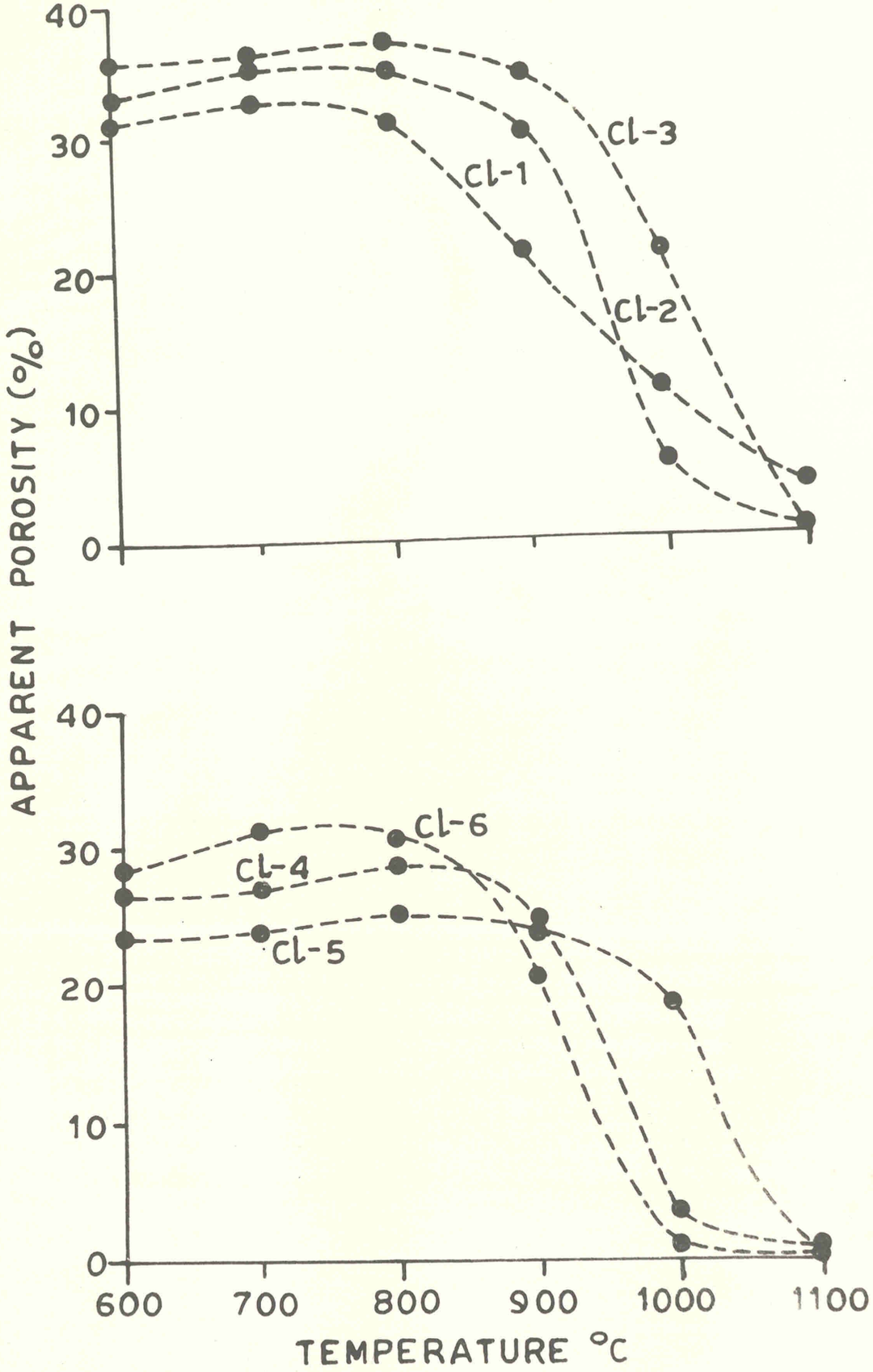

FIG. 5. TEMPERATURE VARIATION OF APPARENT POROSITY OF CLAYS.

800°C corresponds to the decomposition of clay mineral and other hydrous substances, besides dissociation of carbonates and loss of OH water. Further increase in temperatures results in the fusion of alkaline fluxes with alumina and silica forming a glassy matrix which flows into pores and decreases porosity to the minimum, when all the pores are completely filled with molten mass.

It is observed that Cl-2 and 3 are more porous at 600°C because of their study nature. At 1100°C, these clays, however show minimum porosity than rest of the samples except Cl-6, because of the presence of higher amount of fluxes in them which, in general, contribute significantly in lowering the porosity. Minimum porosity of Cl-6 at 1100°C even with minimum quantity of fluxes in it may be attributed to its very fine particle size which fuses more readily at such temperatures and fills the pores, causing decrease in porosity besides its kaolinitic character. Higher porosity of Cl-1 at 1100°C may be attributed to the presence of comparatively low flux content in it. Also, the decrease in porosity or the on set of vitrification is slower in Cl-1 and 6 due to their fine texture. Alkalies present in other clays are comparatively more and thus cause early fall in their porosity, as they combine with silica and alumina at lower temperatures. This factor also accounts for the low porosity of Cl-2 to 5.

(iv) Linear Shrinkage:

All ceramic materials and the articles made therefrom with the exception of some mixtures of clay and silica, shrink when fired causing permanent change in volume, the extent of which depends upon the firing temperature. Although, change in volume can be controlled through the manufacturing techniques, yet the unburnt qualities of the material, such as, the nature, composition, porosity, particle size, previous treatment, the water content of the mass and the pressure applied in shaping it, are the major causes which contribute to its shrinkage. Indeed, these are the factors which control the decomposition and removal of constitutional water, the formation of allotropic form of the material, the chemical reaction, the formation of liquid phase and sintering reactions in the material which, consequently, determine the shrinkage. During decomposition, clays lose water or CO_2 at various temperatures, depending upon the type of the mineral, without causing any appreciable change in volume. On further heating a solid state sintering and crystallization begins resulting in contraction which continues till gamma alumina or distorted spinel phases develop around 750°C in most clays. At higher temperatures mullite, corrundum, etc. start crystallizing, resulting in further contraction.

Linear shrinkage of clays with their

distribution curves are shown in Fig. 6. In most of the cases, change in volume is insignificant upto 800/900°C, possibly due to the absence of any reaction which can contribute to shrinkage. At higher temperatures, the fluxing elements combine with alumina and silica present in the clays, forming a liquid which fills the pores of the mass and cause appreciable contraction. The rate and extent of the contraction in each case varies, depending upon the nature and amount of fluxing oxides, particle size and composition of individual sample. In Cl-1, shrinkage is maximum and occurs between 800 to 900°C, whereas Cl-2 to 5 shrink between 8.4 to 10.2% in the temperature range of 900 to 1000°C. Cl-6 shrinks only 2.5%. Highest shrinkage of Cl-1 at slightly earlier temperature is due to the fact that it has higher silica-alumina ratio than other clays and also contain alkalies to the extent of about 8%. Although alkalies combine with alumina and silica between 700-1100°C in clays, yet it is believed that higher the amount of silica, higher is the temperatures at which the fluxes combine. In Cl-2 to 5, this combination occurs at slightly higher temperatures due to higher silica content in these clays. As Cl-6 contains minimum amount of fluxing oxides and higher alumina and quartz content, it shows least shrinkage. It is believed that both quartz and alumina act as non-reactive skelton and reduce the shrinkage.

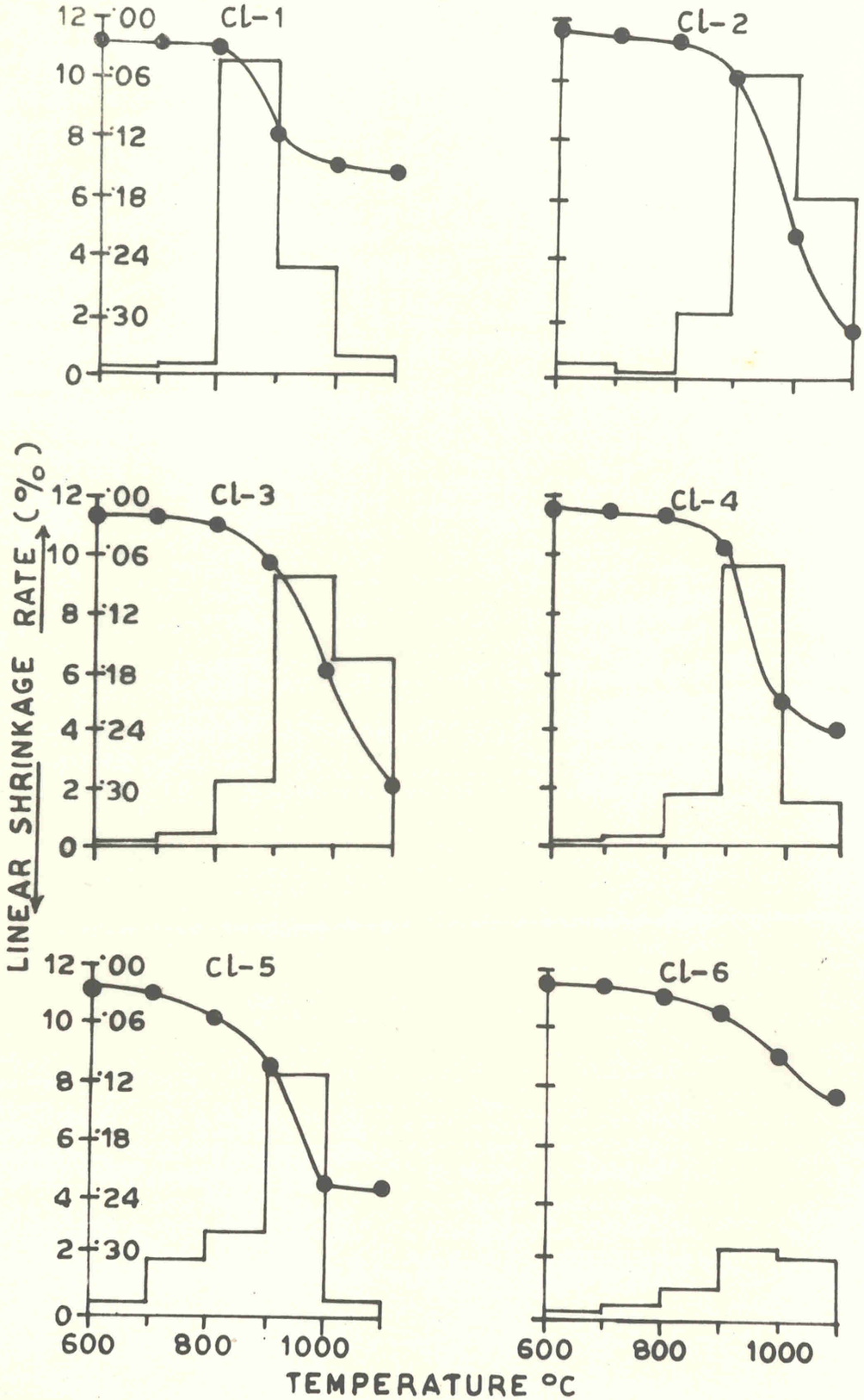

FIG. 6. TEMPERATURE VARIATION OF LINEAR SHRINKAGE OF CLAYS.

Furthermore, since Cl-1 to 5 are Ca-Mg based bentonites, they give comparatively higher shrinkage. Comparatively higher content of sodium alkali, a very powerful fluxing agent present in Cl-2 and 3 also add to their higher shrinkage. Also, they are coarse varieties with higher porosity and hence give high shrinkage.

3.2 MINERALOGICAL PROPERTIES:

Clays, generally, composed of extremely small crystalline particles of one or more members of a small group of minerals known as clay minerals, which are essentially hydrous aluminium silicates, with magnesium or iron proxying wholly or in part for the aluminium in some and with alkalies or alkaline earths present as essential constituents in others. In addition to the clay minerals, clay materials contain varying amounts of non-clayey fraction like quartz, feldspar, calcite etc. Literature provides a number of techniques such as dehydration, differential thermal, x-ray, infrared etc. to identify various clay and non clay minerals present in clays. These techniques have been applied in the present work and results obtained discussed in this section.

(i) Dehydration:

Clay minerals invariably contains some quantity of water in one form or other. The study of dehydration deals with the amount and the rate of water

loss, as well as, the temperature at which loss takes place. In general, during dehydration significant changes in the structure of clay minerals do take place.

Dehydration curves (Fig.7) of most of the clays, in general, show considerable initial loss of weights. Cl-1 loses about 21% of its weight upto 200°C, followed by Cl-5 and 4 which lose 12.2% and 11%, respectively. While in Cl-2 and 3, this loss is low and lies between 8 to 9%, Cl-6 shows minimum loss of weight in this temperature region. It is considered[213] that this initial loss of weight is mostly due to the removal of the interlayer water, usually present between silica sheets and is contingent upon the nature of the adsorbed ions and the preheat treatment of the samples, e.g. the amount of drying, relative humidity etc. Montmorillonites, generally, show high loss of weight at low temperatures and it appears that Cl-1,5 and 4 should possess higher percentage of this mineral than Cl-2 and 3, in which low loss of weight is apparently because of their highly siliceous nature. These clays, therefore, retain much less quantity of water depending upon their silica content and consequently should possess lower percentage of clay mineral. The cation exchange capacity of these samples also show that Cl-1 has higher montmorillonite content followed by Cl-5 and 4. Chemical analysis data indicate highest percentage

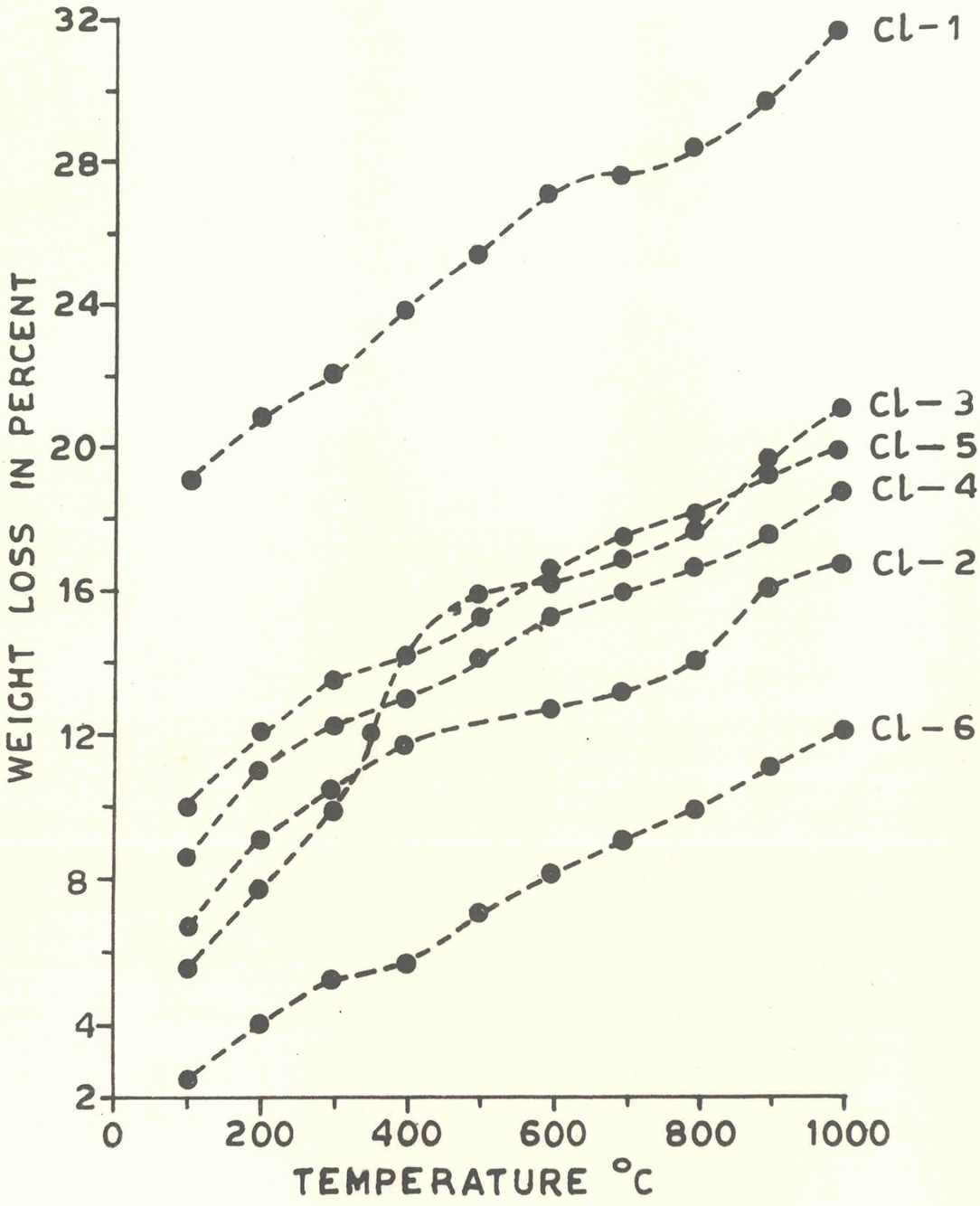

FIG. 7 DEHYDRATION CHARACTERISTICS OF CLAYS

of silica in Cl-2 followed by Cl-3. Cl-6, however, gives loss of interlayer water which is comparable to the values, generally, shown by kaolinite and illite[100,221]. Least value of cec, as well as, non swelling behaviour of Cl-6 also suggest the presence of kaolinite and illite in it.

The general trends of the curves i.e. the variation in loss of weight at low temperatures and rather abrupt loss of OH water beyond 350°C indicates[221] the micaceous nature of the clays. Variation observed in the temperatures region corresponding to the loss of OH lattice water suggests the presence of illite, rather than biotite or muscovite. Being clay mineral micas, illites[222], generally, show such variations in the loss of OH water at low temperatures. This behaviour of illite is unlike well crystallized micas, such as, biotites and muscovites, in having some interlayer water as a result of fewer interlayer cations, less bond between the layers, less uniform orientation of successive layers and even the difference in composition within the silicate layers itself.

Variation in the temperature of OH loss and the absence of any distinct break between the temperatures of the loss of the last interlayer water and begining of the loss of OH lattice water, once again

indicates the presence of montmorillonite mineral in Cl-1 to 5. In these clays, hydroxyl loss begins around 300/400°C and dehydration is complete around 900°C, as expected in montmorillonites and illites. Furthermore, it is observed that in Cl-1 to 5 a distinct shoulder appears around 800 to 900°C, the temperature at which third endothermic peak appears in their differential thermal curves suggesting[223] the presence of montmorillonite in them. Cl-6 does not show either shoulder or S-shaped feature, as it also does not give any third endothermic reaction. Maximum loss of water in Cl-6 between 400 to 600/650°C may be attributed[101] to the presence of kaolinite in it. Beyond 600/650°C, the moisture is lost gradually upto 900°C, where dehydration is essentially complete.

(ii) Differential Thermal Analysis:

This technique has been extensively used for the identification of constituent minerals in clays, which undergo exothermic or endothermic reactions at different temperatures appearing in the form of peaks in thermograms.

The differential thermal curves of clays have been shown in Fig. 8 and the peak temperatures recorded in Table-6.

The first low temperature endothermic reaction which is prominent in all clays occur in the temperature range of 170-190°C, except Cl-1 in which

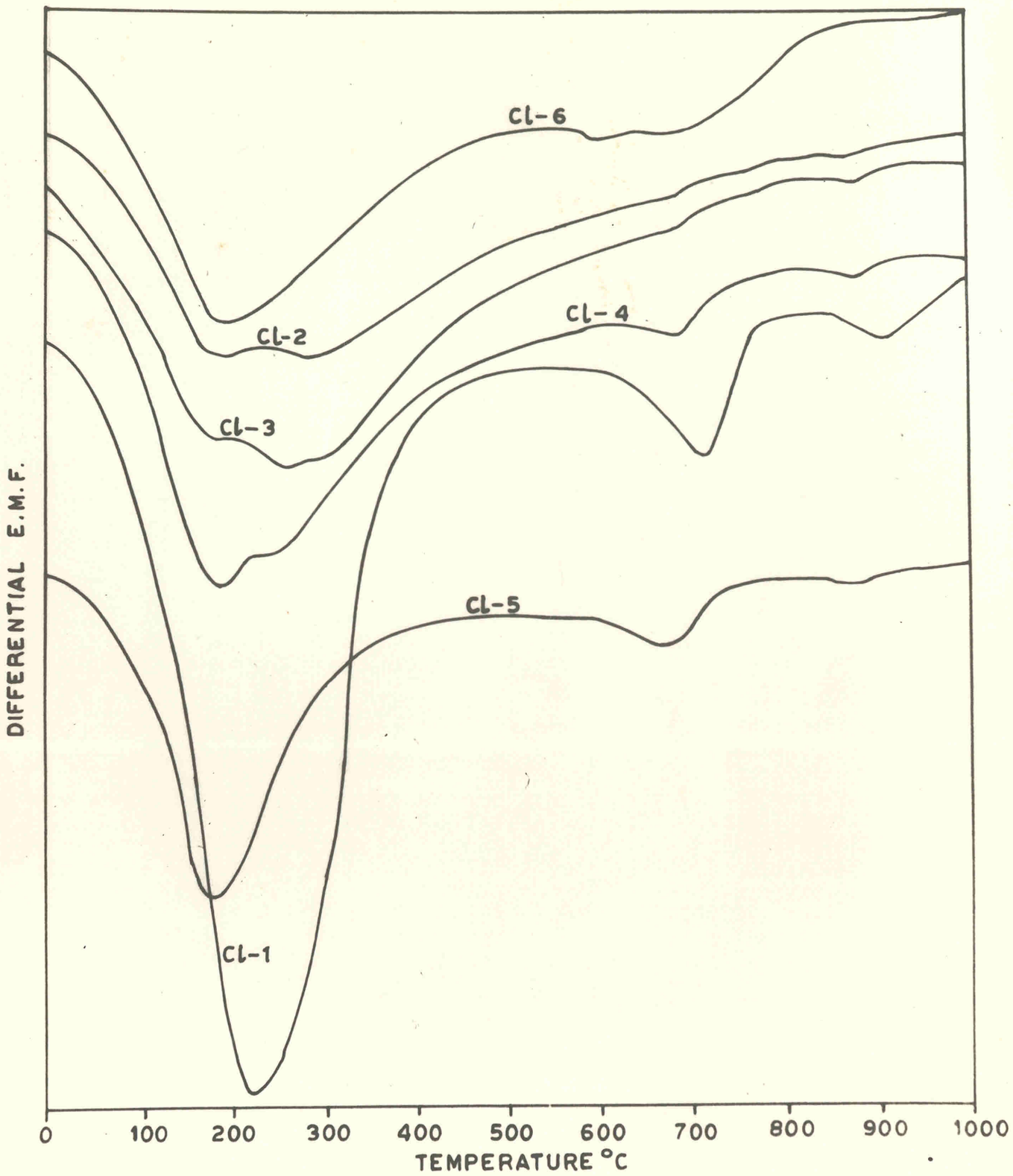

FIG. 8. DIFFERENTIAL THERMAL CHARACTERISTICS OF CLAYS

TABLE - 6

The Peak Temperature of D.T.A. Curves

S.No.	Ist Peak	IInd Peak	IIIrd Peak
C1-1	220°C	720°C	918°C
C1-2	175°C, 285°C	680°C	880°C
C1-3	170°C, 250°C	690°C	895°C
C1-4	190°C	695°C	890°C
C1-5	180°C	697°C	890°C
C1-6	180°C	600°C	925°C

case it appears at 220°C. While Cl-1,5 and 4, in general, give sharp and relatively symmetric peaks in decreasing order of magnitude, Cl-2 and 3 show rather broad and less intense peaks having low symmetry. Dual character of this peak in Cl-2 and 3 is more prominent than Cl-4 and 5. This endothermic peak in clays corresponds to the removal of non-constitutional water which is either absorbed on the surface of the particles or present in the interlayers. The size and character of this peak is contingent upon the nature of the adsorbed ions and pretreatment of the sample. While in air dried samples this peak appears around 100°C, peaks between 150-200°C are also observed, if water molecules are in stronger association with clays. In such cases 100°C peaks are completely removed. Peaks resulting from the loss of hygroscopic water may be prolonged and accentuated, and persist even upto 300°C in many alumino-silicates, sometimes due to the short term grinding. It is considered that mechanical breakdown which occurs by the fractured corners of the crystals, expose free valencies which absorbs and hold water molecules more tightly than hygroscopic water. The forward shift in the temperature of the first peak, thus corresponds to the temperature at which this water is driven out.

Comparatively large magnitude and better symmetry of first endothermic peak in Cl-1,4 and 5 indicate

that these clays contain larger content of interlayer water and are more orderly in structure than rest of the clays. Broad and low intensity endothermic reaction in Cl-2 and 3 suggests their low moisture content, high silica percentage, little clay mineral and poor crystallinity[224]. These observations are in conjunction with the chemical and x-ray analysis data of the clays. Dual nature of this peak can be explained on the basis of the absorption of ions on the surface of the clays and their effect on the absorbed water. It is considered that the larger of the maxima is due to the dehydration of the cations, and lesser of the maxima to the loss of water from the surface of the clay mineral away from the hydrating cations[225].

In all the clays first endothermic peak is very prominently observed as in fire clay minerals e.g. montmorillonite or halloysite group of minerals. Chemical analysis data, however, rules out the possibility of the presence of halloysite mineral in any of the clays. Also, none of the clays crack at elevated temperatures as halloysites do.

Second endothermic peak in Cl-1 and 6 appears at 715°C and 600°C respectively, but in other clays it appears around 680-697°C. While Cl-1 gives relatively sharp reaction followed by Cl-5, 4 and 6, only slight depression appears at this temperature in Cl-2 and 3.

Presence of this peak at 600°C in Cl-6 followed by an exothermic effect indicates the presence of kaolinite and illite in it[124] besides its low magnesium content and minimum loss on ignition.

Third endothermic peak, though of much smaller magnitude, appears in all thermograms, except Cl-6, which shows only upward trend of the curve. Third endothermic peak which corresponds to the removal of last traces of water from clays appears at 918°C in Cl-1 and around 880-895°C in other clays. Grim and Bradley[229] suggest that structure of many montmorillonite, persists even upto 800/900°C and this endothermic reaction may be correlated to the destruction of the lattice. While Page[239] attributes this peak to the loss of OH water bound with magnesium in octahedral coordination, Mc.-Connel[231] has correlated the reaction to the ions of hydroxyls which are in the silica layer in tetrahedral configuration. Third slight endothermic reaction between 850 to 950°C is also shown by illites.

Thus position, symmetry and intensity of peaks observed in differential thermal curves suggest that montmorillonite is the principal clay mineral present in Cl-1 to 5, though associated with varying amounts of illite. Order of crystallinity decreases from Cl-1 to 5,4,3 and 2. Cl-6 appears to be a mixture of kaolinite and illite.

Second endothermic peak is considered to be related to the removal of the water of the lattice. The temperature, symmetry and magnitude of this peak is very important in the diagonsis of the minerals. In montmorillonites, although this peak appears at 700°C, a wide variation in the temperature of this peak has been observed due to degree of crystallinity, chemical composition and the particle size[226,227]. In general, relatively small amounts of iron and magnesium replacing aluminium causes a reduction in the temperature of this reaction and so do the poorly crystalline samples. Even variation in the position of cations in the octahedral packing and hence variation in the nearness to hydroxyl ions affect[228] the bonding strength of OH and hence the energy necessary for its release.

From the magnitude and the symmetry of second endothermic peaks, followed by an upward trend, it appears that Cl-1 is better crystalline followed by Cl-5,4,3 and 2, respectively which give comparatively broad and low intensity peaks. Only slight depression observed in Cl-2 and 3 at this temperature indicate that they have little clay mineral present in them and should also show low loss on ignition, low magnesium and high silica content, as compared to other clays, the observations which are fairly compatible with their chemical analysis data.

(iii) X-Ray Analysis:

Silicate minerals are, in general crystalline in character though their structure and degree of crystallinity may vary from mineral to mineral. Each crystal contains SiO_4 tetrahedron as essential constituent alongwith octahedra of trivalent or divalent ions of Al^{+3}, Fe^{+3}, Mg^{+2} etc. arranged in different ways. The identification of minerals by x-ray analysis has been extensively employed and is based on the principle that each crystalline substance has its own characteristic atomic structure which diffracts x-rays in a characteristic pattern. Comparatively, electron diffraction technique is less widely used as it has to be supplemented with electron microscopy, so as to correlate the morphology of clay mineral particles with their crystal structure.

As clays are admixtures, the singling out of clay minerals from wide range of crystalline materials by x-ray technique has certain difficulties due to structural similarities between many of the clay minerals, as well as, their deviations from strict three dimensional regularity. Also the method does not give encouraging results for amorphous and glassy substances.

The x-ray diffractograms of the samples under investigations are given in Fig.9. The intensities of lines as estimated visually, alongwith their spacings are recorded in Table-7.

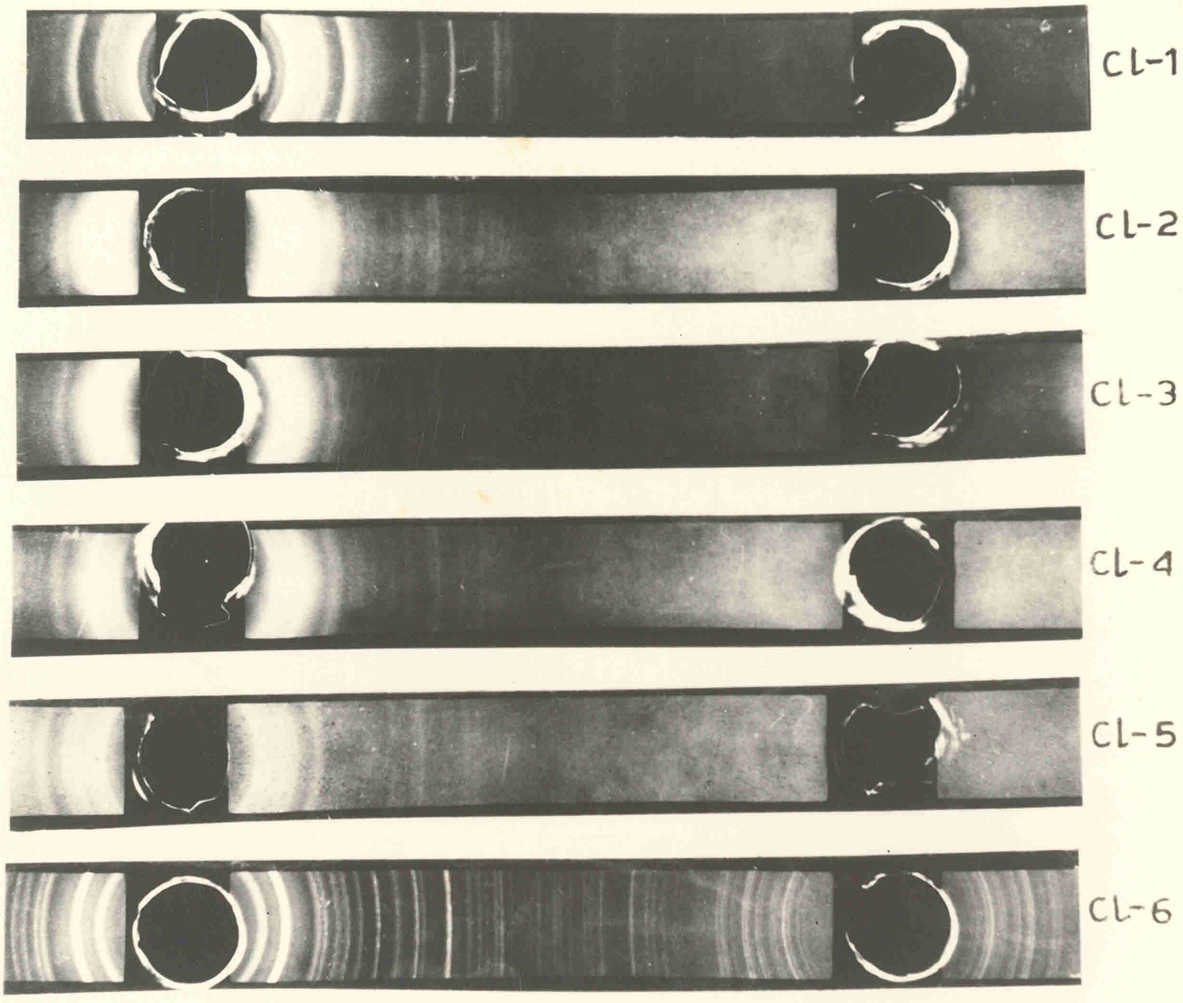

FIG.9. X-RAY POWDER DIFFRACTION PATTERN OF CLAYS.

TABLE - 7

X-Ray Diffraction Data of Clays

Cl-1		Cl-2		Cl-3		Cl-4		Cl-5		Cl-6	
dA°	I	dA°	I	dA°	I	dA°	I	dA°	I	dA°	I
15.13	100	15.57	75	15.13	60						
		9.72	40	10.28	40						
4.39	30	4.44	25	4.43	15B	4.30	30	4.43	35	4.12	55
3.31	4	3.31	25	3.26	40B	3.47	12	3.29	10	3.35	100
						3.22	40				
3.05	7					3.11	25	2.97	10		
2.51	35B	2.49	15B	2.52	30B	2.58	20B	2.56	12B	2.52	25
				2.22	5	2.21	5	2.25	2	2.39	15
										2.17	17
				1.98	5	2.12	5			2.07	18
										1.96	22
		1.80	5	1.81	5	1.80	2			1.80	30
1.67	12	1.67	5B	1.67	15			1.66	1	1.64	13
		1.52	5B	1.52	15	1.50	1	1.47	9	1.52	30
1.48	25	1.49	7B	1.48	10	1.46	18	1.43	1	1.48	15
1.36	3	1.33	5B	1.36	5	1.34	7			1.38	2
										1.36	40
1.28	12	1.28	5	1.27	5	1.27	1	1.26	5	1.21	2
1.24	12					1.19	2			1.16	50
										1.14	10
										1.06	20

It is evident from the data that Cl-1,2 and 3 show their first principal reflection line between 15.13 to 15.57 A^{o} indicating the presence of montmorillonite in them. The reflection lines corresponding to spacings lying between 4.39 - 4.44 A^{o} and 1.46 - 1.49 A^{o} are observed in the diffractograms of all the samples except Cl-6. These lines further asserts that montmorillonite is predominently present in these samples though in varying amounts. The difference in basal reflections obtained in the samples may be attributed to their different state of hydration, depending upon the regularity and the thickness of the water layers between the silica sheets. In Cl-1 reflection lines of comparatively higher intensity appear because of the presence of maximum exchangeable cations in it, as shown by base exchange capacity of this clay. Rather diffused pattern of Cl-2 to 5 indicate more phases, as compared to Cl-1, owing to the presence of higher content of Na^{+} and K^{+} and octahedral hydrates of Ca^{++} and Mg^{++}. It is believed[232] that with water and inorganic cations, montmorillonite complexes show marked influence of the cations on the interlayer separation and the interleaving hydrates with different spacings, giving rise to non integral series of orders and therefore diffused scattering. With Na^{+}, unit layers in montmorillonites are completely separated, but with Ca^{++}, the separation is

incomplete[188,233]. Further, interlamellar cations influence the arrangement of water molecules also. Presence of Na^+ or K^+ do not give rise to stationery regions and consequently basal reflections become diffused.

The reflection lines with atomic spacings lying between 3.22 - 3.35 A^o and 2.49 - 2.58 A^o observed in all the samples correspond to the presence of micaceous minerals and other impurities. Although Bradley and Grim[234] suggested that the reflections in the region 4.4 and 2.6 Kx can be used to distinguish micas of one, two and three unit cells, yet it has not been possible to do so because of very low intensity and shift in the reflection lines. The basal reflections so obtained are the composite adjacent reflections of different orders of the different layers and their position and intensity varies with the relative abundance of the different individual layers. The reflection lines with positions at 9.72 A^o and 10.28 A^o are observed in Cl-2 and 3, respectively indicating the presence of illite in them.

Diffraction data of Cl-6 reveals the presence of quartz. The presence of poorly crystalline kaolinite, as confirmed by dehydration, differential thermal and other characteristics of this clay, could not be established by this technique. It is believed[235] that the presence of even small amount of quartz in a clay is sufficient to

interfere with the detection of other minerals, particularly when present in small proportions or in poorly crystalline state. Thus the x-ray diffractogram of Cl-6 could not clearly reveal the presence of other minerals except quartz.

(iv) Infrared Analysis:

I-R analysis of clays has been carried out to identify the constituent minerals and supplement the results obtained through, Dehydration, D.T.A. and X-ray techniques. The absorption spectra of clays in the range of 2-15 micron is given in Fig. 10. The position of the peaks and band centres with their relative intensities as estimated visually, is recorded in Table-8.

It is seen that some of the absorption features are identical in all samples, except Cl-6, indicating the presence of some common mineral constituents in them. Between 2-8 micron, all spectrograms show absorption peaks located at about 2.85, 3.05, 3.50, 4.30, 6.10, 6.80 and 7.20 micron and a broad band of varying width from 8-10 micron. While Cl-6, gives an intense doublet at about 12.35 and 12.70 micron, other clays give moderate to weak intensity absorption peaks between 10 to 14 micron, before showing a gradual increase in the transmission towards longer wavelengths.

Although, the individual assignment of bands observed in clays with different atomic groupings is yet

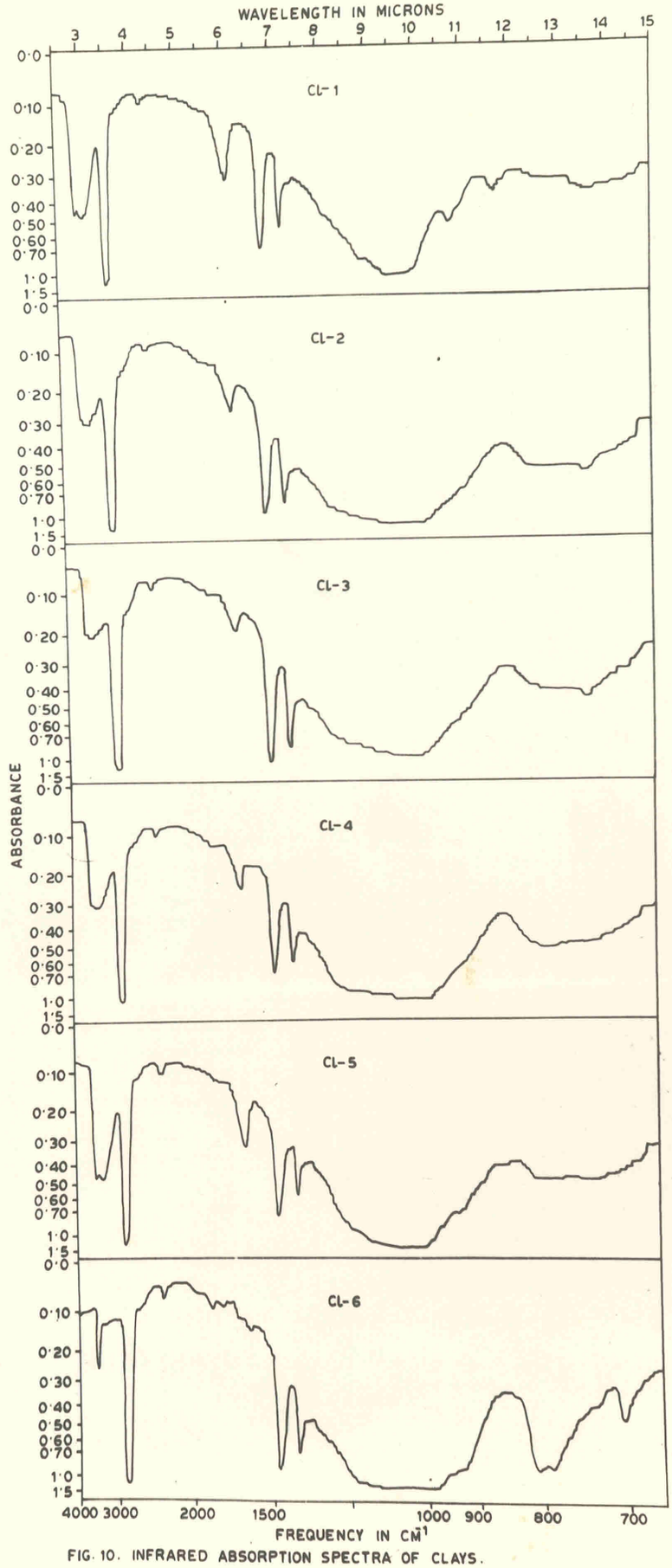

FIG. 10. INFRARED ABSORPTION SPECTRA OF CLAYS.

TABLE - 8

Infrared Analysis Data of Clays

S.No.	2-4 micron	4-6 micron	6-8 micron	10-12 micron	12-14 micron	Beyond 14 microns
Cl-1	2.85 M	4.30 VVW	6.10 W	10.85 M		
	3.05 M		6.80 S	11.75 W		
	3.55 VS		7.20 M			
Cl-2	2.85 W	4.30 VVW	6.10 W	11.05 M	13.50 MB	14.25 W
	3.10 W	6.80 S				
	3.50 VS		7.15 S			
Cl-3	2.90 W	4.30 VVW	6.05 W	10.90 W	13.60 MB	14.20 W
	3.05 W		6.75 S			
	3.50 VS		7.20 S			
Cl-4	2.90 W	4.30 VVW	6.05 W	11.00 W		14.15 W
	3.05 W		6.75 S			
	3.50 VS		7.20 S			
			7.85 W			
Cl-5	2.85 W	4.30 VVW	6.05 W	10.80 M		14.30 W
	3.05 W		6.75 S			
	3.50 VS		7.20 S		12.35 S	14.20 M
Cl-6	2.85 W	4.30 VVW	6.15 VW		12.70 S	14.40 W
	3.05 VW	5.30 VVW	6.80 S			
	3.50 VS	5.55 VVW	7.20 S			

W - Weak, M-Medium, MB- Medium Band, VW- Very Weak

S - Strong, VVW - Very Very Weak, VS - Very Strong.

not well decided, it is believed[135,136] that the absorption band at about 2.85 micron is due to hydroxyl groups in the structure i.e. free hydroxyls; at about 3.05 micron to hydrogen bonded hydroxyl and at 6.1 micron to absorbed water. It is interesting to note that in Cl-6, unlike other clays, the amplitude of the absorption peak due to lattice hydroxyls is much larger than that due to bonded hydroxyls. Also, this clay gives a large reduction in absorption peak at 6.10 micron. The absorption maxima at 2.85 and 6.10 micron are more pronounced in case of Cl-1 and 5, suggesting that these clays have greater capacity for water absorption perhaps owing to the presence of higher percentage of montmorillonite content in them. These observations are also in conformity with higher base exchange capacity and swelling behaviour of these clays. The observed discontinuity in Cl-6 may be due to the presence of illite present in this sample.

The bands centred at 3.50, 4.30 and 7.20 micron are the characteristics[236] of Nujol, used for embedding the samples and, therefore, are not diagnostic of any mineral. The absorption peak at 6.80 micron is noticeable in all spectrograms and corresponds to the presence of illite. However, the greater intensity of this peak is un-understandable, as illites generally show weak absorption peak at such wavelengths. A weak absorption

at 7.65 micron observed only in case of Cl-4 may be assigned[134] to the hydrated water.

The distinction between absorption due to silica tetrahedra and alumina octahedra has not been clearly made, although a number of frequencies have been suggested[237] for montmorillonites. Spectra of various silicates, of which clays are representative, have been defined[137] by the main absorption bands between 9-10 micron. The bands in the region of 8-9 micron have been ascribed to tetrahedral SiO linkage, whereas between 9-10 micron due to octahedral alumina. Stubican[238] has suggested that SiO linkage is represented by the bands in the region of 8-10 micron, whereas octahedral alumina between 10 to 11 micron. The broad bands observed between 8 to 10 micron, thus represent tetrahedral SiO linkage and octahedral alumina.

Although absorption peaks corresponding to montmorillonite, illite and muscovite lie in the range of 9-10 micron, they appear similar except that muscovite gives a pronounced absorption peak at 9.35. Also, montmorillonite cannot be easily distinguished[134] from illite because of very narrow difference in the peak position of the two minerals. In case of clays, due to the presence of other mineral impurities, it is all the more difficult to identify these minerals only on the

basis of absorption peak between 9 to 10 micron. Thus the broad bands observed in spectrograms between 8-10 micron could not identify or differentiate between montmorillonite and illite.

Very weak to weak absorption bands are perceptible towards larger wavelengths. The distinct bands at 10.85 and 11.75 micron in Cl-1 are observed, perhaps due to the presence of montmorillonite in it. Although, Cl-5 also show an absorption peak of moderate intensity at 10.80 micron corresponding to montmorillonite, this peak has very low intensity and shifts towards longer wavelengths in Cl-2 to 4. The absorption bands at 13.50 micron in Cl-2 and 13.60 micron in Cl-6 with moderate intensity correspond to the presence of illite or kaolinite or both. Although, Adler et al[237] attributed this band to the presence of kaolinite, nontronite, halloysite and illite, the chemical and differential thermal analysis of these clays rule out the possibility of the existance of halloysite and nontronite in these samples. A very weak absorption peak observed at 14.2 micron, with the exception of Cl-1, indicate the presence of illite in them. Infrared spectrum of Cl-6 in the wavelength region of 12 to 13 micron is significantly different from others and gives an intense and well resolved doublet, with position of absorption bands at 12.35 and 12.70 micron, indicating the presence

of quartz. The absorption peaks at 14.20 and 14.40 micron in Cl-6 correspond to the presence of illite and kaolinite, respectively in this clay.

Although I-R spectra of clays which represent particular atomic groupings and their vibrations at particular wavelengths are diagonastic of the mineral constituents in the region of 2-15 micron, a wide variation in the position and intensity of the characteristic peaks of various minerals which they represent, has been reported[237]. Variations observed in the spectral features of clays may be attributed[133] to the presence of varying amounts of constituent minerals in each sample, the difference in their particle size and degree of crystallinity. Samples having narrow particle size distribution, with maximum particle diameter smaller than the frequency used, give best spectra.

Since it is not always easy to identify all constituent minerals in clays only on the basis of I-R analysis, as clays are invariably admixtures of minerals, the results obtained from other techniques such as Dehydration, Differential thermal and X-ray analysis when supplemented, reveal that Cl-1 to 5 are mixtures of montmorillonite associated with illite and other clay mineral impurities present in varying proportion and Cl-6, is a mixture of kaolinite, quartz and illite.

3.3 ELECTRICAL PROPERTIES:

From the very existence of solids, one can draw two general conclusions: (a) that in a solid there must be forces of attraction acting between atoms and molecules which keep them together and (b) the forces of repulsion must also exist between constituent atoms, as large external pressure is needed if one has to compress a solid to any appreciable extent.

These forces are electrostatic in nature and essentially determined by the way in which the outer electrons of the composing atoms are distributed in space. As a matter of fact, the physical properties of solids are determined by the distribution of electrons in space. Although, there is no unique way to categorise solids since it would depend upon the exact subject matter, as well as, the view point of the worker, yet one can classify them on the basis of forces acting between the constituent particles, into five categories (a) metallic (b) ionic (c) covalent (d) molecular and (e) hydrogen bonded. Since this classification is merely empirical one and in view of our subject matter, it will be interesting to briefly discuss the electrical behaviour of only first three types.

(a) In metals, conduction is a property of valence electrons which are mobile within the solid due to the overlapping of the atomic state functions. If the

solid is perfectly crystalline, electrons can traverse with complete ease within the solid without undergoing any collisions. On the application of external field, these electrons get accelerated and go to higher energy states even with small absorption of energy. Increase in the velocity of electrons give rise to charge transport and hence electric current. In perfect crystalline solids, increase in the average velocity of charge carriers is relatively high so that charge transport is rapid and resistivity low. In poorly crystalline solids, however, the increase in velocity is not very high due to collisions and hence low conduction. It may be mentioned that high conductivity in metals is the basic property of the structure of valence band or empty states which are immediate adjacent to filled states. The conductivity of metals decreases with the increase in temperature due to the disordering effect of heat which increases the number of collisions.

(b) In ionic crystals, electrical conductivity is far less than that of metals. Also unlike metals, ionic conductivity increases with temperature. These observations indicate that charge carriers in ionic crystals are different than those responsible for conduction in metals. While conduction in metals is due to the motion of electrons, in ionic crystals it is due to the diffusion of ions. In

this type of solids, electrons are so tightly bound in the filled shells that they can not move to any appreciable extent in an external electric field. A basic characteristic of ionic crystals is that the charge transport takes place due to the motion of the charged ions, where not only charge but also mass is transported. Diffusion occurs predominently by lattice vacancies. In the absence of electric field, jumps of individual ions are at random in all directions with no net flow of the charge in any direction. Under the influence of field, more ions jump in one direction than the other, resulting in net transport of charge, as well as, mass. It is this diffusive nature of conduction which accounts for low value of conductivity in such solids and also its negative temperature dependence.

Absence of conductivity due to electrons indicate that in ionic solids, unlike metals, top most levels are all full and there is no empty state immediately adjacent to fermi level. Furthermore, the separation in energy between filled and unfilled states is by far larger than in metals so that even at high temperatures only few electrons are excited and go over to the empty states.

(c) In covalent crystals, conduction varies over a wide range e.g. Diamond is an excellent insulator whereas Germanium is good conductor. A pure semiconductor like Silicon is very poor conductor of electricity at room

temperature, unlike metals. Also its conductivity increases with temperature. In good covalent crystals conduction is due to the transfer of charge carriers among themselves, as in case of ionic crystals. However, in some cases, conductivity is electronic. Some impurities, if present, increase the conductivity; while others decrease it. Such a change in conductivity, however, does not in any way depends upon the flow of electrons as in metals but number of charge carriers due to the presence of impurities. Most of the insulators are classified as ionic crystals, which are never pure elements but compounds having a narrow phase in binary phase diagram. Also such crystals may show variation in stoichiometric composition like Ferrites.

The physics of these three different classes of solids is extremely different, and it is often misleading to treat them within the same structure. However, because of the further complication that mixed ionic-covalent solids are extremely common, such a structure must be developed. It is an appalling fact that ceramics, by and large, fall into this mixed class.

Ceramic materials on firing produce a suitable quantity of glass bond, in addition to the principal constituents. A glass is a complete solution of two or more inorganic compounds usually silicates, formed at elevated temperature by the solubility of one of these

compounds in the other. The property of glass varies with the rate of cooling, as well as, its chemical composition. In most refractories, it is the properties of the glass which actually determine[169,170] their electrical behaviour. Clay is essentially an alumina-silica system, which after dehydrating at 700°C, has the composition ($Al_2O_3 2 SiO_2$) and probably consists of amorphous silica and alumina intimately mixed. If heated beyond this temperature, glassy phase appears with subsequent development of mineral crystallites of various types, depending upon the clay. The firing treatment which can be controlled, can greatly affect the mineral constituents and, therefore, the electrical properties. Thus, it is the chemical composition of the material which is more important than the mineral composition in determining its electrical response.

(i) Electrical Conductivity:

Variation in conductivity of clay pellets in the temperature range of 800 to 1000°C has been plotted in Fig. 11 with 1,2 and 3 hours soaking period. Trends of the curves indicate that initially, conductivity increases rather slowly upto 850/900°C in all samples, before showing sudden rise upto 1000°C. The maximum value of conductivity attained at 1000°C varies from clay to clay, being highest in Cl-6 and lowest in Cl-1.

Slow rise of conductivity upto 850/900°C is due to the premelting stage of the fluxes and rather

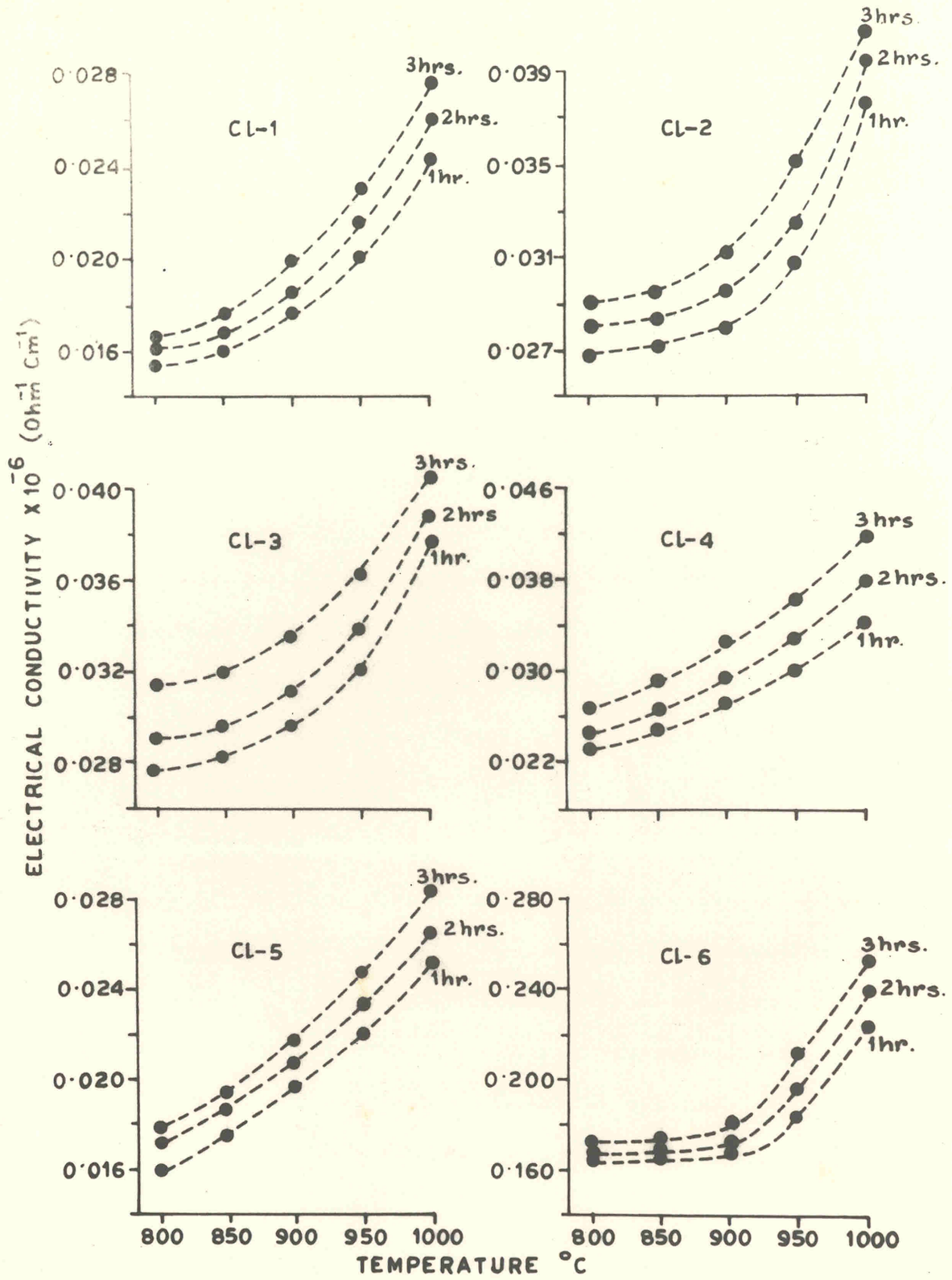

FIG. 11. TEMPERATURE VARIATION OF ELECTRICAL CONDUCTIVITY OF CLAYS.

random movement of ions from one position to another in the lattice. As the temperature is raised, a certain fraction of ions will attain thermal energy sufficient to pass into vacant or interstical sites, thus causing increase in conductivity. This rise in conductivity which is comparable to densification data, of the samples (Table-10), may also be attributed to the fact that the contact areas of particles merge and form glassy matrix in which the ionisation of its constituents does not appreciably increase with temperature[239]. However, the conductivity of glassy phase so produced increases with the increase in temperature due to increase in the velocity of the ions[240] as a consequence of decrease in the viscosity of the medium in which they move. Also, the crystalline phase so developed adds to the ease with which current flows. Littleton and Morey[241], however, reported that the resistivity of glass decreases with temperature in much the same way as its viscosity. Increase in soaking period increases the conductivity. Although, some decrease in conductivity is expected at higher temperatures and soaking periods due to the decrease in the defects in compacts, yet the enhancement in conductivity observed suggests that densification is more predominent a factor here, which decreases the contact resistance between crystallites.

The maximum conductivity of C1-6 may be attributed to the highest percentage of titania in it. It is

believed[166] that TiO_2 is known to be a reduction semi conductor i.e. it can exist with an oxygen content less than the stoichiometric ratio. To maintain electroneutrality[168] in the region of an oxygen vacancy, some Ti^{+4} ions accept electrons. Thus titanium ions are present in two valence states, electron exchange occurs resulting in an increase in conductivity. Cl-2 and 3 show comparatively higher conductivity than Cl-1,4 and 5 for all soaking periods due to the presence of greater percentage of alkalies[169] in them, which being seated in holes in the structure and having substantially higher mobility than the silicate groups tend to take intermediate position between silica tetrahedra. Sodium ions because of their smaller molecular volume enhance conductivity more significantly than potassium ions. The increase in conductivity is however observed to be direct proportion of sodium ion concentration[242]. Also, the lesser percentage of alumina in Cl-2 decreases the viscosity of melt and hence the resistivity of the material. Minimum conductivity shown by Cl-1,4 and 5 may be ascribed[243] to the higher contents of CaO and MgO, which by virtue of their large size and higher charge are not easily mobile and fit into and plug up migration paths through the lattice decreasing conduction. Although it is believed[157] that fluxes decrease the resistivity, yet no direct relationship could be established between the two. For example, Cl-6,

which has minimum percentage of fluxes show higher conductivity, than C1-5 with higher content.

A narrow gap between the conductivity values of C1-1 to 5 is perhaps due to the reason that they all belong to same mineralogical group, although associated with varying amounts of other similar clay mineral impurities. The variation observed in conductivity values of sintered compacts may be attributed to various factors[160] such as; the degree of crystallinity, chemical composition, the specific surface conduction of particles and contact resistance between them which also effect conductivity, as much as, the number and amount of impurities present in each case. Most of these factors are unidentified.

It has been observed that the conductivity of clays is fairly compatible with their porosity data (Table-11). As the porosity decreases with increase in temperature and soaking period, the conductivity increases. Higher conductivity of C1-6 followed by C1-2 and 3 may also be assigned to their comparatively higher porosities.

(ii) Dielectric Constant:

Dielectrics consist of atoms, molecules, and ions which have the property of being unable to provide free conduction electrons. Thus, a particular dielectric material may be characterised by limited movement of charged particles or orientation of polar molecules when an

external electric field is applied. A system of conductors separated by some dielectric material constitutes a condenser, the capacity of which largely depends upon the intervening material. The dielectric constant is defined as the ratio of the capacitance of a condenser filled with the material in question to that when it is empty. The dielectric constant of a single crystal or glass results from electronic, ionic and dipole orientation contributions to the polarizability. The electronic polarization arises from movement of electrons relative to the nucleus in an atom or ion under the action of external electric field and is being widely observed in all materials solid, liquid or gaseous. The ionic polarizability results from the displacement of ions of opposite sign from their regular lattice sites under the influence of applied field and also from the deformation of the electronic shells resulting from the relative displacement of the ions. Most of silicates and aluminates of interest in ceramics contribute to the polarization resulting from this kind of ion displacement[244,245]. In addition, polycrystalline and polyphase aggregates, such as, sintered ceramics exhibit an interfacial or space charge polarization arising from the difference in the conductivity of various phases present which manifests itself in high dielectric constant.

Variation of dielectric constant of clay compacts with temperature and soaking period is plotted in Fig. 12. The dielectric constant of all the specimens show an upward trend with the increase in temperature and soaking period possibly due to the development of crystalline order and grain growth[246], besides an increase in the ion and crystal imperfection mobility resulting in higher capacitance. Also, at higher temperatures, d-c conductivity effects which increase exponentially with temperature, become important. The combined effect is that the dielectric constant increases with increasing temperature, corresponding to both ion jump orientation and space charge effects resulting from the increased concentration of charge carriers. However, the effectiveness of charge carriers in giving an increased dielectric constant depends critically on the electrode materials, polarization effects at the electrodes, and the resulting space charges.

Comparatively lower values of Cl-2 and 3 may be attributed to their sandy nature and the presence of higher percentage of alkalies, as well as, flux impurities in them[247] which concentrate at the crystallite surfaces causing a capacitance drop and hence dielectric constant. As expected from the ion size, for a constant mole ratio the dielectric constant decreases in the order $Li^+ > Na^+ > K^+$.

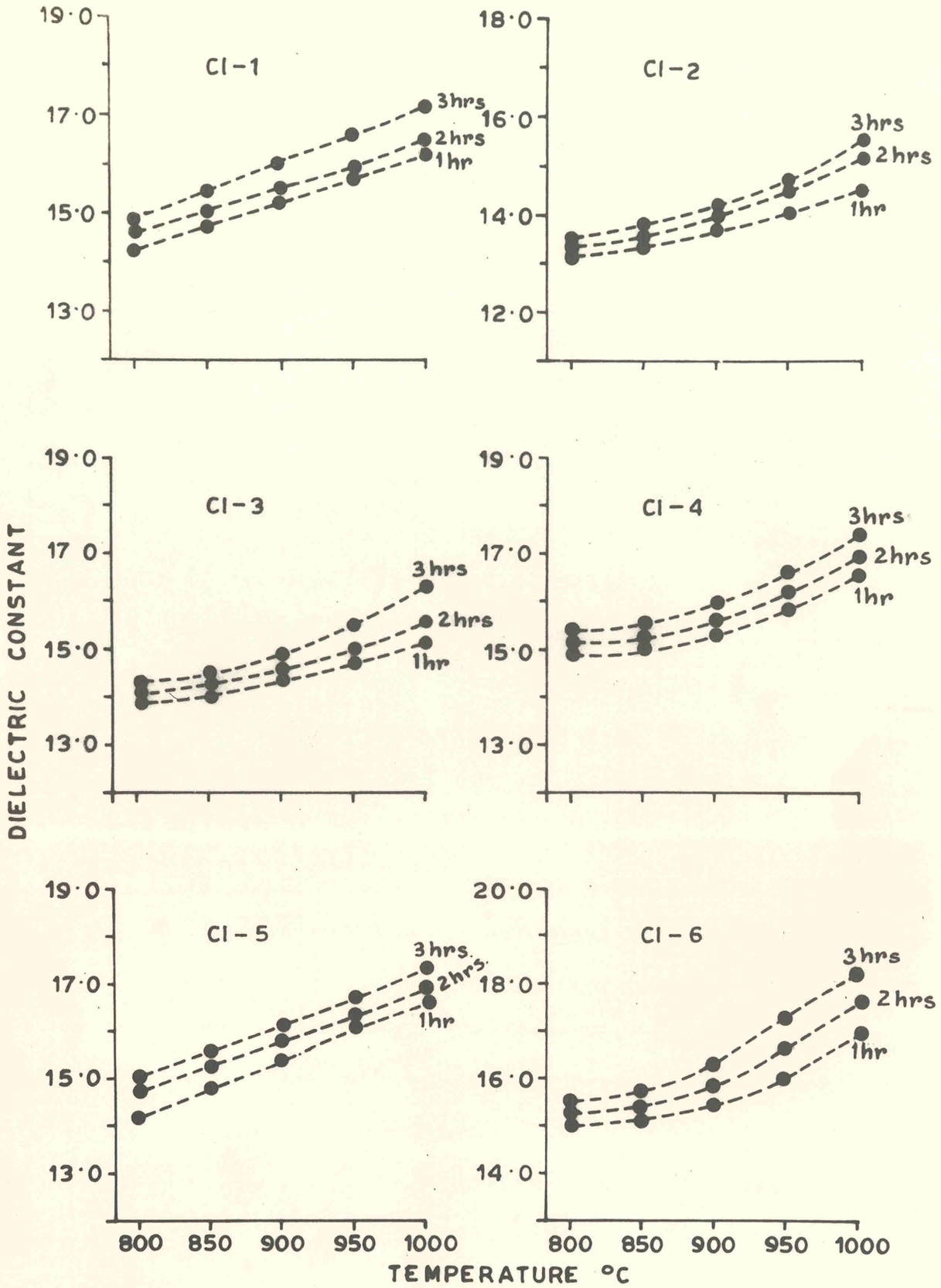

FIG.12. TEMPERATURE VARIATION OF DIELECTRIC CONSTANT OF CLAYS.

Higher dielectric constant value of Cl-6 may, however, be assigned[248] to the higher content of TiO_2 which promote sinterability besides the low percentage of fluxes in it. Also, its finer texture and better crystalline order than rest of the samples would help in developing crystalline phase dispersed in lower dielectric constant matrix at elevated temperatures causing high dielectric constant value. Thus the observations reveal deleterious effect of fluxes and beneficial effect of titania on the dielectric constant of the specimens.

Although lower dielectric constant value of Cl-1 to 5 may also be ascribed to the presence of montmorillonite in them, yet no exact relationship has been established between the percentage of montmorillonite content and dielectric constant of samples. The presence of quartz in Cl-6 and its kaolinitic character contribute to the higher dielectric constant value.

Increasing trend of the dielectric constant of clays appears in agreement with their fall in porosity (Table-11). Cl-6, though fine clay has low percentage of fluxes gives comparatively high porosity and hence dielectric constant at elevated temperatures.

(iii) Dielectric Loss:

The amount of power losses in a dielectric under the action of applied voltage is commonly known as

dielectric loss. Because dielectric materials always possess some degree of conductivity, dielectric loss is observed both in direct current flow and in alternating fields. The distinction is that for direct current flow, the loss depends only on the conductivity, but in the alternating fields, loss may take place with displacement currents also. In polar dielectrics, di-pole molecules rotate under the action of an external electric field overcoming the forces of internal friction of matter, which is attended by the expenditure of a part of electrical energy and its conversion into heat. However, in non polar dielectrics, absorption currents can be attributed to the inhomogeneity in the electrical properties of a dielectric, the formation of space charges in a dielectric under the action of an external electric field and other causes which initiate the processes or redistribution of charges with time in the volume of the dielectric. The power dissipation in an insulator or capacitor is directly proportional to the dielectric loss factor $\epsilon \tan \delta$. Consequently, this factor is of great concern for many applications of ceramic materials. Indeed, the main advantages of ceramics as dielectric is that this loss factor is small compared to that of other available materials such as plastics. Energy losses in dielectrics result from three primary processes.

(1) Ion migration losses

(a) D-C conductivity losses

(b) Ion jump and dipole relaxation losses

(2) Ion vibration and deformation losses

(3) Electron polarization losses.

The electron polarization losses give rise to adsorption and colour in the visible spectrum, while ion vibration and deformation losses are significant only in infrared region. The major factor affecting the ceramic materials is the ion migration losses which tend to increase as the temperature is raised. The dielectric losses of single crystals are small, whereas in glasses, it vary over a wide range depending upon their structure and composition.

Dielectric loss of clays with temperature and soaking period have been plotted in Fig. 13. It has been observed that dielectric loss increases with the increase in temperature and soaking period[249] due to increase in the conduction of residual and absorption currents, besides the ion jump relaxation between two equivalent ion positions. Also, the rise in temperature and the resulting drop in viscosity exert a double effect on the amount of losses due to the friction of rotating dipoles. On the one hand, the degree of dipole orientation increases, and on the other hand, there is reduction in the

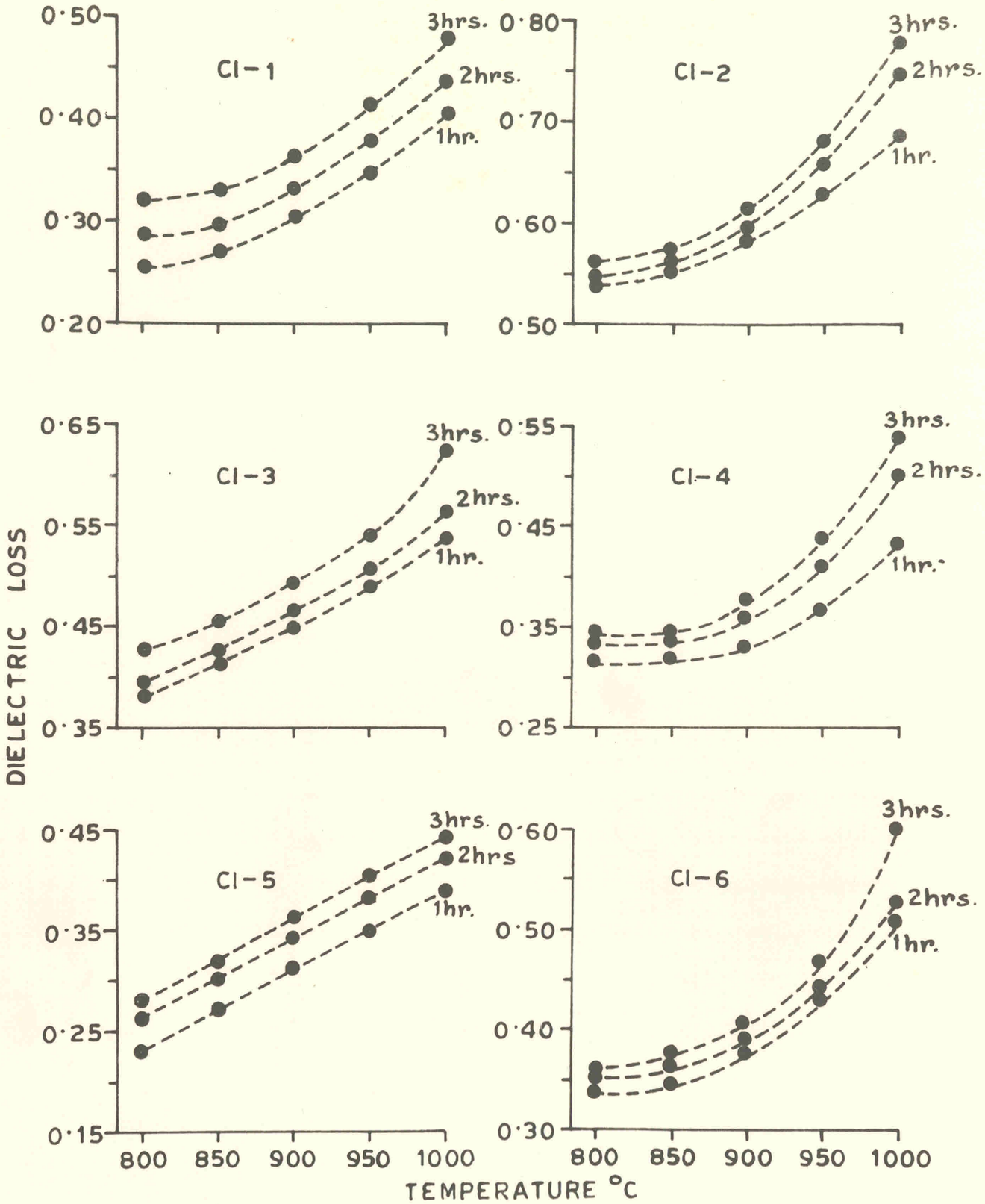

FIG.13. TEMPERATURE VARIATION OF DIELECTRIC LOSS OF CLAYS.

energy required to overcome the resistance of the viscous medium, when the dipole rotates through a unit angle. It has however been agreed that the composition of the glassy matrix so produced at elevated temperatures is the main contributor to the dielectric losses, which increases exponentially with temperature[250].

Observations on dielectric loss of clays indicate that Cl-2 gives comparatively high value, followed by Cl-3, than rest of the samples because of the presence of higher percentage content of alkaline oxides in them which makes the silica network, having each ion held tightly in place, a less rigid and allow to expand it. The network becomes more open and there are larger interstices which permit alkali ions to participate in dielectric loss processes. The order of mobility of alkali ion is $Li^+ > Na^+ > K^+ > Rb$ and the dielectric losses follow in the same order. Under the influence of potential, the alkali ions move from one void to next in a zigzag manner causing high dielectric loss[173]. Comparatively low loss in Cl-1 and 5 may be attributed to the presence of higher content of CaO and MgO which prevent[251] the easy mobility of alkali ions by filling up critical sites through which these ions normally pass. Also, it is believed[252] that higher the alkali-silica ratio, lesser would be the dielectric loss. With the exception of Cl-6, this ratio is

found fairly compatible with dielectric loss in these clays. C1-6, although show least alkali-silica ratio, yet it gives high dielectric loss which may be ascribed to higher alumina content[173], besides the presence of minimum amount of alkalies in it.

The order of observed porosity of clays is, well comparable to their dielectric loss data.

(iv) Dielectric Strength:

This property of a dielectric indicates its ability to withstand large field strengths without electrical breakdown. At low field strengths there is certain d-c conductivity corresponding to the mobility of a limited number of charge carriers related to electronic or ionic imperfections. This d-c conduction increases as the field strength is increased. A stage will come when the field emission from electrodes makes available sufficient electrons for a burst of current which produces breakdown channels, jagged holes, or metal dendrites bridging the dielectric and rendering it unstable. The point of breakdown generates a spark or an electric arc which can fuse, burn and crack the dielectric. After the voltage is taken off, a solid dielectric may exhibit a trace of breakdown in the form of a punctured, fused or burnt through hole, generally speaking, of an irregular shape.

The dielectric breakdown of insulating materials takes place in two ways[253] (i) electronic and (ii) thermal. In electronic breakdown, failure occurs when a localized voltage gradient reaches some value corresponding to intrinsic electrical breakdown. Electrons within the structure are accelerated by the field to a velocity that allows them to liberate additional electrons by collision. This process continues at an accelerating rate and finally results in an electron avalanche which corresponds to breakdown. It may also be developed as a result of inelastic displacement of bound charges in a dielectric under the action of external field. Thermal breakdown is caused by local overheating arising from electrical conduction. The local conductivity increases to the point where instability occurs and permits high current with resulting fusion and vaporisation causing a puncture of the specimen. In this case it is not necessary that the entire volume of the dielectric be heated for a breakdown to take place. It is enough to heat any one spot of a dielectric, in which losses are intensified in view of its inhomogenity but the mean temperature of entire volume of dielectric differs from original one.

Dielectric strength of clay pellets is given in Table-9. It is seen that the variation in dielectric

TABLE - 9

Dielectric Strength (Volts/mm) of Clays

Temp. / S.No.	800°C			850°C			900°C			950°C			1000°C		
	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3hrs
Cl-1	1500	1510	1510	1540	1570	1580	1630	1650	1710	1740	1770	1830	1870	1930	2170
Cl-2	1210	1230	1240	1280	1320	1350	1390	1420	1450	1470	1520	1560	1630	1660	1750
Cl-3	1370	1390	1390	1430	1460	1490	1520	1570	1590	1640	1670	1700	1780	1820	1930
Cl-4	1600	1600	1610	1620	1640	1670	1780	1800	1810	1830	1850	1920	1990	2080	2300
Cl-5	1560	1570	1580	1610	1630	1680	1790	1840	1860	1870	1910	1940	1980	2110	2310
Cl-6	1910	1910	1920	1930	1940	1940	1950	1970	1970	1990	1990	2000	2200	2280	2450

strength with temperature, as well as, soaking period is very small between 800-850°C, but the effect is very much marked at higher temperatures. In Cl-6, however, dielectric strength does not alter appreciably with soaking time. Observed increase in dielectric strength of samples with temperature and soaking period may be attributed to the development of better and denser crystals in the matrix[246]. It has, however, been suggested that at higher temperatures and soaking periods, dielectric strength depends critically on the conduction characteristics and consequently on the composition.

Cl-1 and 4 show comparatively high dielectric strength than Cl-2 and 3, possibly due to the low percentage of iron content in them[254]. Lower dielectric strength of Cl-2 and 3 may be ascribed to the higher amount of alkalies in them besides their sandy nature. In Cl-5 though iron oxide content is highest, it has low percentage of al-kalies. Maximum value of strength in Cl-6 may be attributed to the presence of higher percentage of alumina and comparatively better crystalline structure of this clay. Also, low alkali content in it add to its dielectric strength. Comparison of observations with chemical analysis data of clays confirm the deleterious effect of iron and alkaline oxides and the beneficial effect of alumina on the dielectric strength of the compacts.

TABLE - 10

Density (gm/cc) of Clays

Temp. / S.No.	800°C			850°C			900°C			950°C			1000°C		
	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs
Cl-1	1.96	1.98	2.02	2.01	2.03	2.06	2.12	2.18	2.21	2.28	2.36	2.42	2.68	2.71	2.87
Cl-2	1.78	1.81	1.82	1.86	1.88	1.91	2.02	2.07	2.12	2.48	2.50	2.60	2.57	2.62	2.70
Cl-3	1.82	1.84	1.88	1.90	1.92	1.99	2.06	2.10	2.15	2.22	2.28	2.35	2.52	2.60	2.78
Cl-4	1.88	1.90	1.95	1.96	2.02	2.08	2.10	2.18	2.26	2.32	2.36	2.48	2.64	2.71	2.82
Cl-5	1.92	1.94	1.98	1.95	1.99	2.04	2.06	2.13	2.21	2.25	2.31	2.43	2.66	2.72	2.84
Cl-6	2.54	2.55	2.57	2.55	2.57	2.58	2.58	2.59	2.60	2.66	2.68	2.70	2.84	2.89	2.95

TABLE - 11

Porosity (%) of Clays

Temp. / S.No.	800°C			850°C			900°C			950°C			1000°C		
	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs	1 hr	2 hrs	3 hrs
Cl-1	20.34	19.42	18.30	15.44	14.32	12.57	10.50	9.84	7.29	7.34	6.72	4.75	3.21	2.04	1.70
Cl-2	23.14	20.53	19.61	16.49	14.53	12.47	10.95	9.54	7.08	7.12	5.50	5.03	3.53	2.83	2.12
Cl-3	22.03	20.10	18.57	15.63	14.54	13.07	10.12	9.73	7.50	6.50	5.32	4.97	3.77	2.52	1.92
Cl-4	20.08	19.31	18.15	15.91	13.90	13.10	9.66	9.17	6.80	6.42	4.71	4.53	3.02	2.04	1.32
Cl-5	21.72	19.92	18.62	15.61	14.72	13.00	10.52	9.12	6.83	7.15	5.12	4.62	3.41	2.10	1.55
Cl-6	24.12	21.62	19.54	15.24	14.51	12.47	9.61	8.52	5.49	5.54	4.04	3.10	4.00	3.02	2.55

Dielectric strength values are compatible with the corresponding porosity data of the samples (Table-11) and the development of densification in them due to increase in temperature, as well as, soaking period. C1-2 and 3 show lower dielectric strength possibly due to their comparatively higher porosity than rest of the samples except C1-6, which possibly tends to give variation in the local electric field and yields low values. A sample with 14% porosity was found to have dielectric strength about half that of sample with 5% porosity[255]. Least densification of C1-6 which is kaolinitic in character associated with quartz, besides low amount of fluxes accounts for the marginal change in its strength upto 900°C followed by a sharp increase in its value.

At present the knowledge of the mechanism of electrical behaviour of ceramic materials does not permit a detailed analysis of the result. The effect of impurities as shown by Diepschlag and Wulfestieg[161] and the different porosities and texture of the materials would confuse an attempt to attribute the results exclusively to composition or to structure. There are several other unidentified factors, such as, packing of particles, surface conduction etc. besides the development of various phases at elevated temperatures, which greatly influence the electrical response of samples.

CHAPTER- IV

STUDIES ON THE TRIAXIAL SYSTEM

Investigations presented in this section can essentially be considered as a meaningful extension of the stipulated research programme involving only the physico-chemical and mineralogical studies of some clays, besides their electrical properties which have been presented in previous chapters. Since one of the six varieties of clays studied has been characterised as kaolinitic in character, it was considered worthwhile to prepare a triaxial system using this variety and study its electrical, thermal and mechanical characteristics, besides composition by x-ray techniques. Basic purpose to include this part is to have an idea of the above properties to assess the suitability of the clay for use in ceramic Industry. It is not intended to go into detailed discussions to justify the results obtained, but to see the range in which the values lie. Essential physical properties like density and porosity of the product have also been recorded. Thus, in view of very limited approach only one composition has been prepared and fired at only one temperature and soaking period.

4.1 TRIAXIAL SYSTEM:

Ceramic insulators have been important to our technology and to the ceramic industry for so long that the number of products available and technical literature describing them are vast. Also, these insulators

are unique in low cost of their raw materials, ease of fabrication into wide variety of shapes and sizes and uniform quality of the final product for use under different conditions. The electrical porcelains manufactured, now a days, are quite different from the standard recipes for conventional ones[256]. In modern porcelains, the artificial or natural refractory materials, such as; mullite, sillimanite, kyanite etc. have been introduced into clay compositions instead of quartz and feldspar to give high strength and resistivities at higher temperatures. Recently, compositions having high strength have been developed by adding calcined bauxite.

However, ordinary porcelain is usually made[257] from clay, quartz and feldspar mixed in varying proportions, depending upon the usage of the end product. The primary purpose of these components may be described, rather, roughly in the following way. Clay gives the body, the necessary plasticity during forming, cohesion during firing and strength after firing. Feldspar acts as a flux and forms glass during firing while quartz is a filler which ensures less shrinkage and more stability to the body at higher temperatures.

4.1.1 Changes During Firing

Triaxial bodies pass through several processes on their way to the final product, the most

important being forming, drying and firing. The composition of the body is not determined only by the desired properties of the material in the finished product, but also by the properties required for the body during the different phases of manufacture. The composition may vary considerably according to the purpose of the product.

In the raw state, relatively large quartz and feldspar grains are surrounded by clay crystal plates and stacks. Thus, the contact surfaces consist of quartz-kaolin and feldspar-kaolin, but only exceptionally of quartz-feldspar.

The changes taking place in a system at particular temperature during firing depends upon the chemical and mineralogical composition, nature and type of clay used, besides heat treatment the body is subjected to. When the body is heated, the chemically bound water in the kaolinitic clay is expelled at 500-600°C, giving rise to meta-kaolin phase[106] i.e. $Al_2O_3.2\ SiO_2$. Between 700-1000°C, the mixed alkali feldspars are transformed into homogenous form called sanidine[258, 259]. It has also been shown[260] that meta kaolin phase at 925-950°C condenses to spinel type mullite phase ($2Al_2O_3.3\ SiO_2$) and amorphous silica. Also, in this temperature interval, melt phase begins to form between sanidine and the amorphous silica in the clay relicts. The sintering of the body also starts with the melt formation, very slowly at first, but faster as the

proportion of melt increases and its viscosity is lowered. At about 1000-1050°C, the mullite phase begins to develop[261] in the clay phase relicts from the spinel type phase with discarding of silica. Around 1200°C, the mullite phase also begins to form in feldspar relicts. With further increase of temperature, mullite crystals continue to grow.

The quartz grains are not significantly affected by other components below 1200°C. But above this temperature, the dissolution of quartz grains begins, developing solution rims of crystal free glass. Above 1400°C, porcelain consists of mullite and glass with little content of quartz. The firing range of these compositions is quite long since the viscosity of the liquid phase increases as the amount of dissolved silica increases. In this respect, the flint is contributing to the resultant product and not acting as just a filler.

4.2 EXPERIMENTAL METHODS AND PROCEDURES:

Dry clay (-120 ASTM) was mixed thoroughly with powdered quartz and feldspar in 2:1:1 ratio (by weight). The wet ball milling of the ingredients was done for about 10 hours to form a uniform and thick paste which was subsequently dried at 110°C for 16 hours. Granulation was then carried out by adding appropriate quantity of water and (-40, +80) fraction of the material collected for

preparing samples of different dimensions, as required in various tests. Except for thermal expansion, all samples were fired at 1150°C for 3 hours. Chemical analysis of clay, quartz and feldspar used is given below:-

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	L.O.I. (%)
Clay	59.20	29.35	1.42	1.07	1.45	1.00	0.15	-	6.08
Felds-par	64.25	17.87	0.76	0.08	0.20	-	1.15	12.84	0.35
Quartz	98.20	-	-	-	-	-	-	-	0.02

Procedures followed in determining the various properties are briefly described below:

(i) X-Ray Analysis :

X-ray analysis was carried out in the same manner as described in Sec. 2.2 for clay samples.

(ii) Electrical Properties :

The procedures adopted while determining electrical conductivity, dielectric constant, dielectric loss and dielectric strength of the circular pellets (approximately, 25 mm diameter and 3 mm thickness) pressed at 7000 psi were essentially the same as given in Sec. 2.3.

(iii) Thermal Properties :

Thermal conductivity and thermal expansion of specimens were determine in the following manner:

(a) Thermal conductivity .

An improvised form of Lee's apparatus was

used to determine the conductivity of circular pellets of above dimensions with one face maintained at 100°C (T_i°C), using steam chest as a source of heat. Temperature at the other face (T_2°C) was measured using Cu-Fe thermocouple with metal disc placed on the sample. The radiation loss from the periphery of the sample was, however, minimised using non-conducting cotton wool. Conductivity was calculated employing the relation

$$K = m.s. \frac{dT}{dt} \cdot \frac{x}{A(T_1-T_2)}$$

where m and s are the mass and specific heat of the disc respectively; $\frac{dT}{dt}$, the slope giving the rate of cooling of the disc at temperature T_2; x, the thickness in cms and A, the area of sample in cms^2.

(b) Thermal Expansion.

Expansion-contraction behaviour of cylinderical test samples (approx. 50 mm in length and 10 mm diameter) pressed at 100 Kg/cm^2 was measured using an automatic dialatometer type 402 DA, manufactured by NIZZEK, West Germany, having a controlled heating rate of 5°C per minute. The coefficient of expansion was calculated from the curve and plotted against temperature.

(iv) Mechanical Properties:

Compressive, as well as, transverse strength of the compacts pressed at 7000 psi was determined adopting the following procedure:

(a) Compressive Strength.

Compressive strength of specimens (1 inch cube) was determined by Universal Testing Machine. The load was applied to the specimen without shock and increased slowly until it broke down. The load per unit cross sectional area, which the sample could withstand, was calculated as compressive strength and expressed to the nearest whole number.

(b) Transverse Strength.

Transverse strength of rectangular bar (approx. 9 cm x 1 cm x 1 cm) was measured by placing it over two wedges placed 6 cms apart and applying pressure on the top surface by a third wedge, at a place midway between the length of the specimen. Pressure was increased slowly, till the test piece broke down. Modulus of rupture in lbs/inch^2 was calculated using the relation:

$$T = 3\ WL/2\ BT^2$$

where W is the breaking load in lbs; L,B and T the span length, breadth and thickness of test piece, respectively, in inches.

(v) Density and Porosity:

These properties were determined following the procedures given in Sec. 2.1.2.

But for x-ray analysis and expansion contraction behaviour, all other properties were determined for five specimens and their average values recorded.

4.3 OBSERVATIONS AND DISCUSSIONS:

Observations on the x-ray analysis, electrical, thermal and mechanical properties have been recorded and discussed briefly in sub-sections 4.3.1, 4.3.2, 4.3.3 and 4.3.4, respectively.

4.3.1 X-ray Analysis

X-ray diffraction pattern of the product is given in Fig. 14 and the intensity of lines, as estimated visually with their spacings recorded in Table-12.

The position and intensity of the lines, as evident from the diffraction data, prominently indicate the presence of quartz, as well as, mullite phase. The reflection line corresponding to 4.13 A^{o} suggests the presence of quartz which does not interact and form liquid due to its low reactivity at 1150°C. The position of high intensity line at 3.20 A^{o} is rather controversial. While Roy[262] attributes it to the presence of quartz, others[263, 264] assign to the mullite phase. The reflection lines at 2.39 A^{o}, 2.07 A^{o}, 1.77 A^{o}, 1.50 A^{o} and 1.35 A^{o} assert the presence of mullite. It is believed[265, 266] that the degree of crystallinity, the nature and type of impurities and experimental conditions greatly affect the position and intensity of reflection lines.

It has been suggested[267] that the mullite

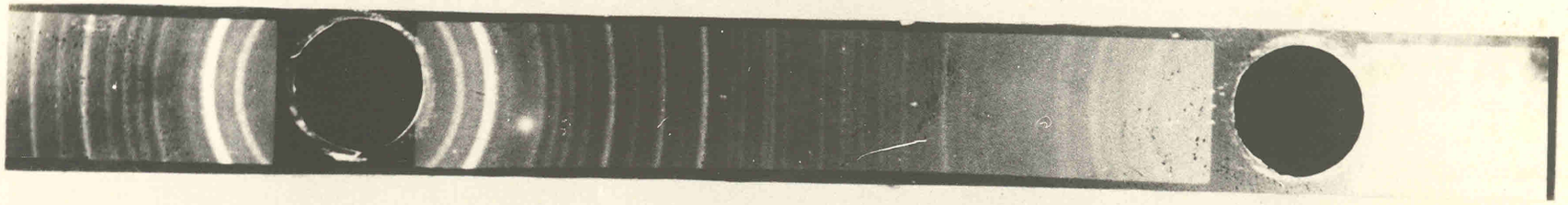

FIG. 14. X-RAY POWDER DIFFRACTION PATTERN OF TRIAXIAL SYSTEM.

TABLE - 12

X-Ray Diffraction Data of Triaxial System

dA°	I	dA°	I
4.13	50	1.91	20
3.24	100	1.77	45
2.83	10	1.62	20
2.39	20	1.50	41
2.22	20	1.42	4
2.07	20	1.38	4
		1.35	47

formation takes place either directly from the dissociation of clay followed by nucleation and crystal growth or from the solution of clay and feldspar with subsequent crystallization. Experimental evidence supporting the role of feldspar in mullite formation is, however, not very strong, though McVay[268] believes that the crystallization starts at the clay boundaries by feldspar grains. Indeed, there is sufficient evidence to show that the dissociated clay forms the first glass phase due to its amorphous nature and highly reactive character[269]. Clay glass reacts with adsorbed salts and other impurities present in the body, forming a glassy matrix before crystallization.

4.3.2 Electrical Properties

The electrical characteristics of ceramic insulators depend upon the nature and type of different phases formed at elevated temperatures, firing conditions, the extent to which high temperature composition is retained on cooling, besides the composition and structure of the clay used. Observations on the electrical behaviour of the triaxial composition have been recorded in Table-13. Indeed, in polycrystalline aggregates which are essentially ionic in character, the contributions to the polarization and hence conductivity, as well as, dielectric constant are due to those ions[244,245] which become more mobile with the melt formation. Although, the development of

TABLE - 13

Properties of Triaxial System

1.	Electrical Properties:	
i)	Electrical Conductivity	0.546×10^{-8} mhos cm^{-1}
ii)	Dielectric Constant	10.20
iii)	Dielectric Loss	0.87
iv)	Dielectric Strength	3745 Volts mm^{-1}
2.	Thermal Properties:	
i)	Thermal Conductivity	0.00692 Cal $cm^{-1} sec^{-1} c^{o-1}$
3.	Mechanical Properties:	
i)	Compressive Strength	13000 $lbs/inch^2$
ii)	Transverse Strength	2260 $lbs/inch^2$
4.	Physical Properties:	
i)	Density	2.32 gm/cc
ii)	Porosity	3.22 %

crystalline mullite phase and grain growth should add to the ease with which current flows and provide better strength to the specimen, yet glass is the most important phase which gives porcelain its fundamental electrical properties. Alkalies which liberate from the feldspar reaction diffuse into clay relicts and decrease the porosity which in turn improves the electrical response. Porosity of the order of 3.22% at 1150°C can significantly lower the dielectric strength of the specimen. Dense packs tend to react less on cooling than do the porous ones. Although, electrical properties are frequently correlated with porosity, yet the effect of porosity is to control the kinetics of compositional changes rather than any direct contribution.

4.3.3 Thermal Properties:

In dielectric materials heat transfer is caused due to lattice vibrations, while the electrons remain fixed and do not contribute significantly. Thermal conductivity of polycrystalline materials depends upon the arrangement and compositions of solid phases together with the pore phase present. The thermal conductivity of the system is comparable to the available data for polyaggregates. It is considered[270] that crystals with complex structures have a greater tendency towards thermal scattering of lattice waves and consequently show low

conductivity. The presence of mullite phase in the product with complex structure provides low mean free path for thermostatic waves causing a reduction in the conductivity. Also, the system has 3.22% porosity, which is yet another important factor[271, 272] to inhibit free conduction. It is believed that while small pores act as a barrier to heat flow, large pores increase the conductivity at high temperatures. Also, the air present in and the radiation across the pores contribute to heat transfer. Since fine pores are unstable at elevated temperatures, it is rather difficult to make high temperature insulating materials from clay compositions.

The changes in volume of ceramic materials with temperature mainly depend upon their structure, besides the chemical and mineralogical composition. The increase in volume may be determined by the increased amplitude of vibrations due to increase in the lattice energy which ultimately results in larger atomic separations causing lattice expansion. The expansion contraction behaviour of triaxial system is plotted in Fig. 15. Initial expansion upto around 400/500°C, considered to be of reversible nature, is due to the presence of kaolin[273]. The increase in the co-efficient between 500 to 600/650°C may be confered to the $\alpha \rightleftharpoons \beta$ transition of quartz. The volume stability observed in the temperature range of

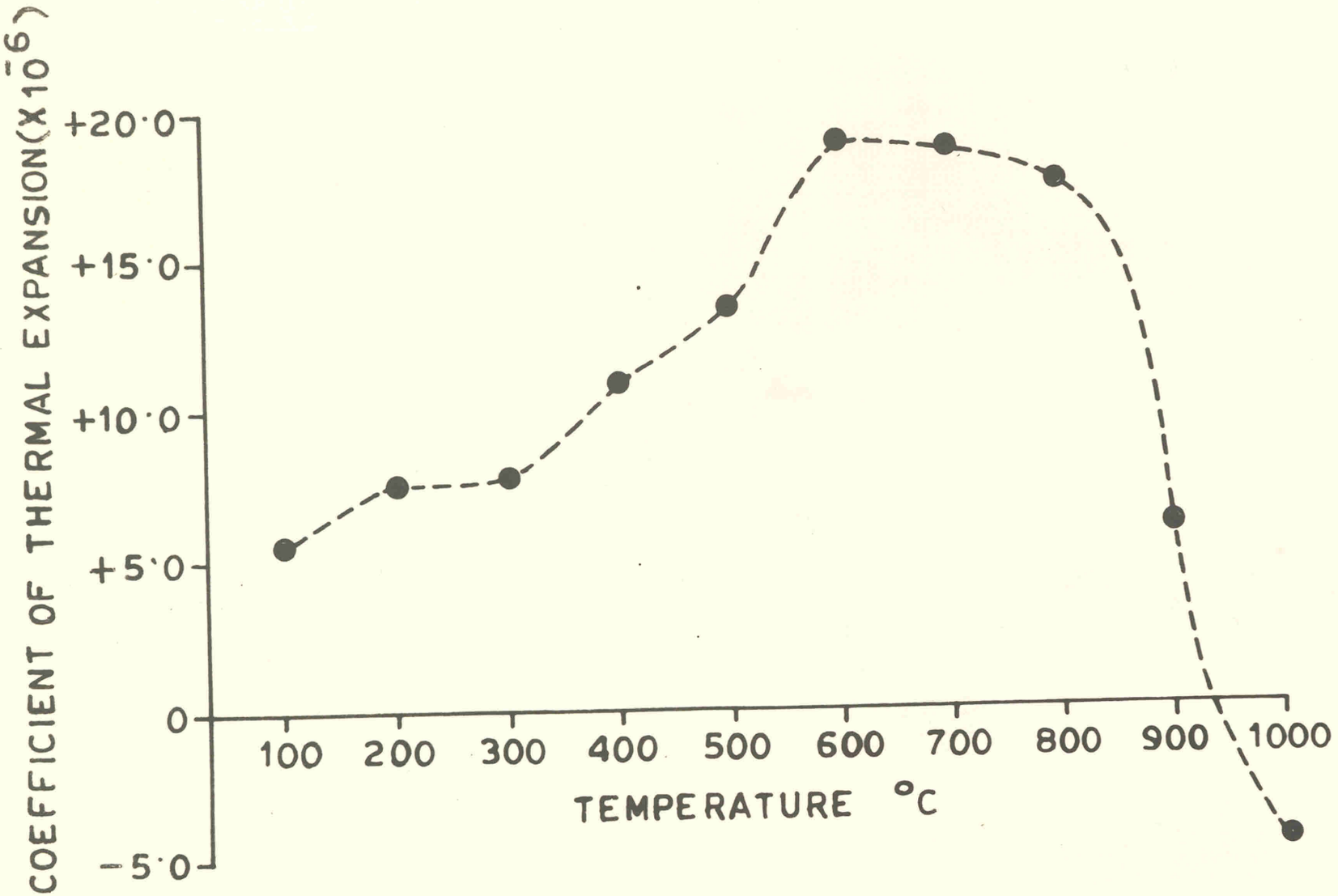

FIG.15. EXPANSION CONTRACTION BEHAVIOUR OF TRIAXIAL SYSTEM.

600/650°C to 800/850°C is possibly due to the fact that the lattice collapse and recrystallisation of the clay mineral is insufficient to counter balance the stabilising influence of the nonplastic components. Beyond 850/900°C alkalies get liberated from the feldspar and form liquid, the quantity and quality of which depends upon the components present in the liquid phase. The liquid so produced enters the voids in the system resulting in sharp contraction, the rate and extent of which will depend upon the stabilising effect of quartz content in the body.

4.3.4 Mechanical Properties

In homogenous materials, rupture usually involves a ripping; whereas in composite materials with hetrogenous grains, fracture plane follows a highly complex path between various mineral phases. In compressive fracture, layers of the body are squeezed together in the direction of applied pressure, while transverse fracture commences on the lower surface and is propogated upwards throughout the specimen.

Compressive strength of the system is observed to be greater than the transverse due to the fact that the ionic components are being forced into closer juxta-position, resulting an increase in the forces of repulsion when an atom can only be separated from its

neighbours by forces which are sufficient to squeez it from its normal position.

There are various factors such as texture, porosity, co-efficient of expansion and contraction, firing condition etc. besides the chemical and mineralogical composition, which affect the strength of ceramic materials. Fine particles, generally, facilitate reactions on firing resulting an increase in strength. During heating, the chemical reaction takes place between mineral components forming liquid which surrounds more refractory grains; on cooling it solidifies and acts as a cement serving to bind the mass together, causing an increase in strength. The development of mullite phase may also provide a mass of interlocking particles, adding to the strength. It is considered[274] that if the mullite is the dominent crystalline phase, the change in the rigidity is less or non existant. Although, there is only a very indefinite relation between porosity and strength of such materials, yet greater strength is incompatible with higher porosity.

The electrical, thermal and mechanical properties of triaxial system studied do not warrant to arrive at and predict specific conclusions based on the factors controlling these properties. It is an appalling fact that polycrystalline aggregates, such as the product

fall into mixed ionic-covalent class of crystals which does not and possibly cannot provide any definite model in relation to various mechanisms operating to control the behaviour of the product. Indeed the development of various phases and complex structure involved make it more difficult to understand and appreciate such mechanisms fully and analyse or interpret the results satisfactorily in a quantitative manner. It may be mentioned that glassy phase is perhaps the most important factor which contributes to these properties. This phase, by itself is dependent upon numerous factors, some of which cannot be even identified adequately.

CHAPTER- V

GENERAL DISCUSSIONS AND CONCLUSIONS

It is, indeed, an appalling truth that the knowledge of physico-chemical properties and the mineralogical composition of a clay mineral is an essential prerequisite for its optimum exploitation in any clay based industry. The determination of these properties will avoid any wasteful and indiscriminate use of the minerals for producing materials of doubtful quality and performance. The study presented in the thesis is, as a matter of fact, the first attempt of its kind in which such a consistent and exhaustive data on the physical, chemical and mineralogical aspects of six clays occuring in Jammu Province of J&K State has been given. The study reveals five out of six samples as bentonitic and sixth as kaolinitic in character though associated with varying amounts of other clay mineral impurities. It has not been possible only to characterise the deposits but also present data on their electrical response. Further, the study also includes investigations on the electrical, thermal and mechanical properties of a typical triaxial system, prepared making use of the only kaolinitic variety by mixing it with quartz and feldspar.

General conclusions based on these investigations may be summarised as under:

All the clays are alkaline in nature, though by varying degrees. While clays from Parmandal,

Jagati and Khanpur slake faster and show higher swelling, Jungle Kali sample is practically non-swelling and also takes much longer time to disintegrate. But for the two bottom layers of Parmandal deposits which are coarse, lean and less plastic; all others are fairly compact, fine in texture and have good plasticity. Workability of all bentonitic varieties, indeed bear a cognizable relationship with water of plasticity, particle size and base exchange capacity. Kaolinitic clay of Jungle Kali with least amount of water of plasticity and swelling character is very good to work at owing to its fine particle size. Viscosity of clays appear directly related to particle size of individual sample. Increase in the concentration of clay in the suspension, as expected reduces the free motion of the fluid increasing the viscosity. Addition of dispersing agents like sodium carbonate and sodium silicate to clay suspension decreases sharply the viscosity to a critical point beyond which it remains constant with any further addition of electrolytes.

Chemical analysis data gives silica-alumina ratio comparable to bentonites for all samples except Jungle Kali. The variations observed in this ratio and other chemical constituents of bentonites is expected due to wide range of substitution within the lattice of such

minerals and the nature and amount of exchangeable ions in them. Base exchange capacity coupled with the swelling behaviour and chemical analysis results assert that except Jungle Kali clay which is kaolinitic, all others are Ca-Mg based bentonites, associated with small amounts of sodium and potassium ions.

Fired properties like density, porosity and shrinkage show significant changes initiating only around 800°C, the exact temperature and the rate of change being dependent upon the amount of fluxes, particle size distribution and non clayey component present in individual case. Alkaline fluxes start melting around this temperature forming a liquid phase which fills the pores and decreases the porosity to minimum, when all the pores are completely blocked. As expected the density at this stage is maximum. Reduction in shrinkage depends upon the quantum of quartz and silica present in the sample which act as non reactive skelton in it. The fired colour of materials is compatible with the colouring agents like oxides of iron and titanium, in which 'd' shells being incomplete and valencies variable, exchange of electrons can easily occur. But for Jungle Kali variety, all others vitrify around 1100°C.

Mineralogical composition as determined by dehydration and differential thermal analysis amply reveal

the presence of montmorillonite and illite in varying proportions in all clays, except Jungle Kali in which the presence of illite could not be unambiguously established, though its kaolinitic character was ascertained. X-ray analysis though in general, supplements these results but fails to show the presence of illite and even kaolinite in Jungle Kali sample due to the presence of quartz which gives intense lines making it difficult to analyse it accurately. Interestingly the diffused pattern of bentonites bear relation to the presence of Na and K and octahedral hydrates of Ca and Mg, which do not give rise to stationery orbits. However, infrared analysis when supplemented with the results obtained by these techniques as mentioned above does confirm that deposits from Parmandal, Jagati and Khanpur contain montmorillonite as principal mineral constituent though in varying amount, associated with illite. Jungle Kali clay could be characterised as a mixture of quartz, kaolinite and illite.

Electrical conductivity, dielectric constant, dielectric loss and dielectric strength increases with temperature, as well as soaking period owing to the increase in the amount of melt and possible development of crystalline phase. Titania enhances the conduction and dielectric constant. Alkaline fluxes add to electrical

conductivity and dielectric loss but affect adversely the dielectric constant and dielectric strength. Oxides of calcium and magnesium, because of their large size, retard the mobility of sodium and potassium ions by filling up the critical sites through which the latter have to pass, decreasing the conductivity, as well as, loss. While iron oxide decreases the dielectric strength, alumina adds to it.

Studies on the triaxial system reveal the presence of mullite and quartz phases through x-ray analysis, though it was difficult to predict whether mullite phase developed directly from the dissociation of clay followed by nucleation and subsequent crystal growth or from the solution of clay and feldspar followed by crystallization. The electrical and thermal behaviour of the product is fairly normal, but its dielectric, compressive and transverse strength is rather poor. Expansion-contraction behaviour reveal $\alpha \rightleftharpoons \beta$ transition of quartz between 500-650°C and rapid contraction beyond 850/900°C due to the liberation of alkalies from feldspar reaction forming liquid.

Although there are numerous factors, which control the physico-chemical, mineralogical and electrical behaviour of alumionosilicates and the products made therefrom, some of which have not been and also are

difficult to identify; yet it is hoped that the investigations providing an extensive data on the various aspects of the properties studied will suggest valuable points for consideration, while making an attempt to select these deposits for their purposeful utilization in any clay based industry.

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